

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



(2)

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : <b>E21B 37/06, C10L 3/00, F15D 1/00, F17D 1/05, 1/02, C09K 7/06, C08F 228/02, 226/06, F17D 1/00</b>		A1	(11) International Publication Number: <b>WO 95/32356</b> (43) International Publication Date: 30 November 1995 (30.11.95)
(21) International Application Number: <b>PCT/US95/06042</b>			(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).
(22) International Filing Date: 10 May 1995 (10.05.95)			
(30) Priority Data: 248,477 25 May 1994 (25.05.94) US 358,140 15 December 1994 (15.12.94) US			
(71) Applicant: COLORADO SCHOOL OF MINES [US/US]; 1500 Illinois Street, Golden, CO 80401 (US).			Published <i>With international search report.</i> <i>With amended claims.</i>
(72) Inventors: SLOAN, Earle, Dendy, Jr.; 2121 Washington Street, Golden, CO 80401 (US). LEDERHOS, Joseph, Paul; 3290 Jay Street, Wheatridge, CO 80033 (US). CHRISTIANSEN, Richard, Lee; 7934 South Pennsylvania Drive, Littleton, CO 80122 (US). PANCHALINGAM, Vaithilingam; 13025 West Second Place #311, Lakewood, CO 80228 (US). DU, Yahe; 2301B Cheyenne Street, Golden, CO 80401 (US). SUM, Amadeu, Kun, Wan; 1117 8th Street, Golden, CO 80401 (US). LONG, Jin, Ping; 4015 Brook Haven Club Drive #804, Dallas, TX 75244 (US).			
(74) Agents: BREYFOGLE, Ross, E. et al.; Sheridan Ross & McIntosh, Suite 3500, 1700 Lincoln Street, Denver, CO 80203 (US).			

(54) Title: ADDITIVES AND METHOD FOR CONTROLLING CLATHRATE HYDRATES IN FLUID SYSTEMS

(57) Abstract

Discussed is a process for preventing clathrate hydrate masses from detrimentally impeding the possible flow of a fluid susceptible to clathrate hydrate formation. The process is particularly useful in the natural gas and petroleum production, transportation and processing industry where gas hydrate formation can cause serious problems. Additives preferably contain one or more five member, six member and/or seven member cyclic chemical groupings. Additives include polymers having lactam rings. Additives can also contain polyelectrolytes that are believed to improve conformance of polymer additives through steric hindrance and/or charge repulsion. Also, polymers having an amide on which a C<sub>1</sub>-C<sub>4</sub> group is attached to the nitrogen and/or the carbonyl carbon of the amide may be used alone, or in combination with ring-containing polymers for enhanced effectiveness. Polymers having at least some repeating units representative of polymerizing at least one of an oxazoline, an N-substituted acrylamide and an N-vinyl alkyl amide are preferred.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## ADDITIVES AND METHOD FOR CONTROLLING CLATHRATE HYDRATES IN FLUID SYSTEMS

### FIELD OF THE INVENTION

The present invention involves a method and chemicals for controlling problems that can be caused by clathrate hydrates, and particularly by gas hydrates, in fluid systems.

### BACKGROUND OF THE INVENTION

Clathrate hydrates are crystalline compounds which occur when water forms a cage-like structure around guest molecules. Clathrate hydrates, especially in the hydrocarbon industry, are often referred to as gas hydrates, or simply as hydrates. Gas hydrates of interest to the hydrocarbon industry, particularly with respect to producing, transporting, and processing of natural gas and petroleum fluids, are composed of water and the following eight guest molecules: methane, ethane, propane, isobutane, normal butane, nitrogen, carbon dioxide, and hydrogen sulfide. Other guest molecules capable of forming clathrate hydrates, although not normally of significant interest to the hydrocarbon industry, include nitrous oxide, acetylene, vinyl chloride, methyl bromide, ethyl bromide, cyclopropane, methyl mercaptan, sulfur dioxide, argon, krypton, oxygen, xenon, trimethylene oxide, and others.

Clathrate hydrate formation is a possibility any place water exists in the vicinity of such molecules, both naturally and artificially, at temperatures above 32°F and below 32°F when the pressure is elevated.

-2-

It is primarily due to their crystalline, insoluble, non-flowing nature that hydrates have been of interest to industry. They have been considered a nuisance, because they block transmission lines, plug Blow Out Preventors, 5 jeopardize the foundations of deepwater platforms and pipelines, collapse tubing and casing, and foul process heat exchangers and expanders. Common examples of preventive measures are found in the regulation of pipeline water content, unusual drilling mud compositions, and large 10 quantities of methanol injection into pipelines.

Hydrates normally form in one of two small, repeating crystal structures. Structure I (sI), a body-centered cubic structure, forms with natural gases containing molecules smaller than propane. Structure II (sII), a diamond lattice 15 within a cubic framework, forms when natural gases or oils contain molecules larger than ethane but smaller than pentane; this structure represents hydrates which commonly occur in hydrocarbon production and processing conditions. Also, at least one other repeating crystal structure is 20 known to exist, and additional structures theoretically could exist.

The structures of both sI and sII are given with reference to a water molecule skeleton, in which guest molecules are encaged, composed of a basic "building block" 25 cavity which has twelve pentagonal faces given the abbreviation  $5^{12}$ . By linking the vertices of  $5^{12}$  cavities one obtains sI, while linking the faces of  $5^{12}$  cavities results in sII. The regions between the linked  $5^{12}$  cavities

-3-

in repeating crystal structures are larger cavities which contain twelve pentagonal faces and either two or four hexagonal faces:  $5^{12}6^2$  for sI and  $5^{12}6^4$  for sII. The water molecules around a cavity are held in place by hydrogen bonds, which attach water molecules to each other to form the cavity. Inside each cavity resides a maximum of one guest molecule. Cavities other than the  $5^{12}6^2$ ,  $5^{12}6^4$ , and  $5^{12}6^4$  cavities, just described, could exist in repeating crystal structures other than sI and sII. Any cavity, however, 10 should have exactly twelve pentagonal faces. Additional information concerning clathrate hydrates, and particularly gas hydrates, can be found in Sloan, Clathrate Hydrates of Natural Gases, M. Dekker, N.Y., 1990, the contents of which are incorporated herein in its entirety.

15 There are four common means of inhibiting formation of or dissociating hydrates, namely: 1) removing one of the components, either the guest molecule or water, 2) heating the system beyond the hydrate formation temperature at a given pressure, 3) decreasing the system pressure below 20 hydrate stability at a given temperature, and 4) injecting an inhibitor such as methanol or glycol to alter hydrate stability conditions so that higher pressures and lower temperatures are required for hydrate stability. The above four common techniques are termed thermodynamic inhibition, 25 because they remove the system from thermodynamic stability, by changes in composition, temperature, or pressure. While the system is kept outside thermodynamic stability conditions, hydrates can never form.

-4-

Recently, new chemical treatments have been proposed for controlling clathrate hydrate problems. For Example, in European Patent Office Publication No. 0457375A1, published November 21, 1991, use of alkyl aryl sulfonic acids is proposed for preventing or retarding the formation of hydrates or for reducing the tendency of hydrates to agglomerate. Additionally, International Publication No. WO 93/25798, published December 23, 1993, proposes the use of polymers of N-vinyl-2-pyrrolidone for inhibiting the growth and/or agglomeration of gas hydrate crystals.

Also, in U.S. Patent No. 4,915,176 by Sugier et al., issued April 10, 1990, a method is proposed for using amphophilic compounds, having a hydrophilic part and a lipophilic part, which are mixed with a fluid to be transported to lower the gas hydrate formation temperature and/or to modify the mechanism of formation of such hydrates. It is reported that such compounds disperse the gas hydrates in the fluid and then prevent their agglomeration. However it is believed that the process would not be effective in a fluid system containing a continuous aqueous liquid phase, that is, for example, an aqueous liquid phase that is not dispersed throughout a continuous organic liquid phase such as in a water-in-oil type emulsion. Therefore, that process would not be effective, for example, in a fluid system containing both a gaseous and an aqueous liquid phase, but containing no organic liquid phase, or a fluid system comprising

-5-

significantly more aqueous liquid phase than organic liquid phase.

Many of these recently proposed chemical treatments are expensive due to the high cost of the chemicals and/or 5 the relatively low effectiveness of the chemicals. International Publication No. WO 94/12761, published on June 9, 1994, describes the use of certain polymers having lactam rings. These additives represent an improvement in both performance and cost, but are still relatively 10 expensive. Also, many of these recently proposed methods are not adequate to control problems with hydrates at the very high pressures and low temperatures that are encountered in many situations, such as during subsea pipeline transportation. For example, subsea pipelines may 15 be operated at pressures as high as 2000 psi or more at temperatures of 40°F or less, but the effectiveness of many hydrate control methods are limited to much lower pressures at low temperatures.

There is a need for new, more effective treating 20 chemicals and less expensive treating methods to address clathrate hydrate problems in fluid systems, particularly those encountered in producing, transporting, and processing petroleum and natural gas fluids.

#### SUMMARY OF THE INVENTION

25 One object of the present invention is to provide a process for preventing clathrate hydrate masses in a fluid stream from impeding flow of the fluid stream, particularly

-6-

with respect to fluid streams encountered in the hydrocarbon industry such as with the production, transportation and processing of petroleum and natural gas fluids.

5 Another object is to provide an economical process for preventing clathrate hydrate problems in fluid systems.

Another object is to provide additives for use in controlling clathrate hydrates in fluid systems, which additives have low toxicity and, therefore, their use is  
10 environmentally desirable.

Another object of the invention is to provide a process for preventing clathrate hydrate masses from agglomerating to form large masses in fluid systems containing a continuous aqueous liquid phase.

15 According to the present invention, an additive is added to a fluid system to prevent clathrate hydrate masses from forming, or to prevent clathrate hydrates that are present, or that form, in a fluid system from agglomerating or otherwise growing to form clathrate hydrate masses that  
20 would be large enough to create problems in the fluid system, such as by impeding the flow of fluids. Preferably, clathrate hydrate masses are prevented from becoming larger than the size of several repeating crystal structure units. In particular, it is believed that the additive interacts  
25 with clathrate hydrate cavities of clathrate hydrate masses in a way that prevents those cavities from participating in the formation of larger clathrate hydrate masses.

-7-

In one embodiment, clathrate hydrate masses are prevented from impeding the flow of a fluid stream by the addition of a ring-containing polymeric additive. One such additive is a polymer having at least some repeating units 5 characteristic of polymerizing or copolymerizing one or more N-vinyl lactam monomers, such as N-vinyl-2-pyrrolidone, N-vinyl- $\delta$ -valerolactam, and N-vinyl- $\epsilon$ -caprolactam. In another embodiment the additive comprises hydroxyethylcellulose. In another embodiment the additive 10 comprises a compound sold under the name "Gaffix VC-713" by International Specialty Products, or comprises a compound having similar attributes.

In another embodiment, an additive comprising at least one five member cyclic chemical group, six member cyclic 15 chemical group and/or seven member cyclic chemical group is added to the fluid stream to prevent clathrate hydrate masses from impeding the flow and, more specifically, it is believed, to interfere with the process by which smaller clathrate hydrate masses form larger clathrate hydrate masses. In one embodiment, the cyclic chemical group is 20 non-aromatic. In another embodiment, the cyclic chemical group comprises a heterocyclic ring, preferably including an internal amide and/or an internal ester group.

In one embodiment, the additive comprises multiple 25 different cyclic chemical groups, preferably with a first cyclic chemical group having a different number of atoms in the ring than a second cyclic chemical group. In another

-8-

embodiment, an additive comprises both a five member cyclic chemical group and a seven member cyclic chemical group.

In another embodiment, clathrate hydrate masses are prevented from impeding the flow of a fluid stream by 5 application of an additive that has a molecular weight greater than about 3,000. Preferably, the additive is a polymer of molecular weight greater than about 10,000 more preferably greater than about 20,000, and most preferably greater than about 40,000. In one embodiment, particularly 10 large molecular weight additives, having molecular weights of one million or more, are used.

In one embodiment, a method for hydrate control is provided using additives that do not have an organic ring. One additive is a polymer having at least some repeating 15 units representative of polymerizing an oxazoline monomer. Other additives include alkoxy compounds, which preferably comprise polyethoxy and/or polypropoxy blocks. One preferred additive is a block copolymer having polyethoxy and polypropoxy blocks. Also, a method is provided for 20 using additives that comprise a polymer having an N-substituted noncyclic amide that is part of a pendent constituent attached to and extending from a polymer backbone. These additives are particularly preferred because they perform substantially as well as many of the 25 ring-containing additives, but are considerably less expensive and, therefore, offer an economic alternative for clathrate hydrate control. One such polymer is poly(N-methyl-N-vinylacetamide). Two particularly preferred

-9-

examples of these additives are poly(N-ethyl acrylamide) and poly(N,N-dimethylacrylamide).

Other preferred additives not requiring the presence of an organic ring have a polymer backbone and a pendent constituent attached to and extending from the backbone, in which the pendent constituent comprises a noncyclic amide with the nitrogen of the noncyclic amide occupying a position in the pendent constituent that is closer to the backbone than is the position of the carbonyl carbon of the noncyclic amide. Preferred additives of this type include polymers of N-vinyl alkyl amides, such as N-methyl-N-vinylacetamide, N-vinylacetamide and N-vinylformamide.

Particularly preferred additives not requiring the presence of an organic ring include polymers having an amide in which at least one of the nitrogen and the carbonyl carbon of the amide has at least one organic group attached having from one to four carbon atoms. Although not completely understood, the presence of a relatively small organic group or groups attached to the nitrogen and/or the carbonyl carbon of an amide may provide a site around which water molecules may cluster in a pseudo-hydrate fashion to prevent the water from participating in hydrate formation. Examples of these particularly preferred additives include polymers of 2-methyl-2-oxazoline; 2-ethyl-2-oxazoline; N,N-dimethylacrylamide; N-ethyl acrylamide and N-methyl-N-vinylacetamide.

In one aspect, the effectiveness of additives can be improved by varying the chemical structure of the additives

-10-

and/or by mixing the additives with other substances. Many of the polymer molecules used in additives for inhibiting hydrate formation appear to be significantly associated with one another when dissolved in an aqueous solution.

5 Also, individual polymer molecules appear to exhibit a compact molecular conformation in solution. The significant association of molecules and the compact conformation of individual molecules both tend to reduce the effectiveness of additives by making it difficult for some functional

10 groups on the polymers to effectively interact with clathrate hydrate masses that may be present in a fluid. Therefore, it appears that the effectiveness of polymer additives could be improved by reducing the association of the polymers with one another and/or by attaining a more

15 extended, and less compact conformation for the individual polymer molecules. Less polymer would be needed to provide the same level of clathrate hydrate control and costs are thereby reduced.

In one embodiment, steric hinderance and/or charge

20 repulsion may be used to reduce association between polymer molecules and to promote extension of individual polymer molecules in an aqueous solution. In one embodiment, the additive comprises a polyelectrolyte. In another embodiment, the additive comprises a polymer having a

25 plurality of lactam rings and a plurality of anionic groups. In one embodiment, a chemical is provided having a plurality of seven member rings and a plurality of anionic groups pendent from a polymer backbone.

-11-

Also, many additives appear to perform more effectively when mixed with another substance. In one embodiment, clathrate hydrate control polymers useful with the present invention are used together with one or more 5 alcohols. In another embodiment, two different polymers, each having a lactam ring, are used together. In a further embodiment, a polymer having at least some repeating units characteristic of polymerizing an oxazoline monomer can be used, preferably by mixing with other additives.

10 One surprisingly effective combination of additives comprises a first polymer having a heterocyclic ring with nitrogen as a hetero atom, which is preferably a lactam ring, and a second polymer having a noncyclic amide, which is preferably an N-substituted noncyclic amide. The 15 combination of the two additives appears to provide a synergistic effect compared to the use of each additive separately. For example, a mixture of VC-713, a lactam-containing polymer, with poly(N-ethyl acrylamide) has been shown under laboratory conditions to be effective at about 2000 psi and 39.2°F, conditions under which neither of the 20 additives is effective when used alone. In one embodiment, a method is provided for using the additives to prevent clathrate hydrate masses in a fluid from forming masses large enough to block fluid flow at a pressure of greater 25 than about 1500 psi and a temperature of lower than about 45°F, such as might be encountered in many subsea pipelines.

-12-

In one embodiment, the additive is used in combination with a high salinity aqueous phase. The presence of a high salinity aqueous phase has, surprisingly, been found to be beneficial for use with many additives and particularly for 5 those comprising a lactam ring.

According to the present invention, The fluid system may comprise, in addition to clathrate hydrate masses that may be present, any combination and relative proportions of a gaseous phase, an aqueous liquid phase, and an organic 10 liquid phase. In one embodiment, the fluid system comprises an aqueous liquid phase and a gaseous phase. In another embodiment, the fluid system comprises a fluid stream that is transported by flow through a conduit. In another embodiment, the fluid system comprises one or more fluid 15 phases from the production, transportation or processing of natural gas or petroleum fluids.

#### DETAILED DESCRIPTION OF THE INVENTION

In one respect, the present invention involves preventing clathrate hydrate formation or controlling the 20 joining together of clathrate hydrate masses in fluid systems to form larger clathrate hydrate masses. The present invention also involves controlling the formation of clathrate hydrates in a fluid system to prevent large clathrate hydrate agglomerates in a fluid system. A fluid 25 stream having clathrate hydrate masses mixed therein, or that is susceptible to the formation of clathrate hydrate masses, is contacted with an additive that prevents

-13-

clathrate hydrate masses from forming a mass or masses that could impede the flow of the fluid stream. Preferably, clathrate hydrate masses no larger than several repeating crystal structure units are allowed to form. Preferably, 5 the additive is at least partially soluble in water.

The present invention is particularly useful in the hydrocarbon industry such as with the production, transportation and processing of natural gas and petroleum. The present invention is useful, for example, to control 10 gas hydrates that could form during extraction of natural gas and petroleum fluids through a producing well, during transportation of the extracted fluids, and during processing of the extracted fluids.

One useful additive comprises at least one cyclic 15 chemical group, also known as a ring group, in its molecular structure, and more preferably, the additive comprises a plurality of cyclic chemical groups, which can be either the same or different. Preferably, the cyclic chemical group is not aromatic. A cyclic chemical group 20 refers to an organic ring structure, which may contain only carbon atoms as members of the ring, or may contain one or more other atoms in a heterocyclic ring such as, for example, atoms of oxygen, nitrogen, sulfur, and/or phosphorus. Preferably, the cyclic group has a polar 25 moiety, which is either a polar atom, such as oxygen or nitrogen, in the ring, or a polar substituent, such as an oxygen atom, attached to the ring, or both. More preferably, the cyclic chemical group is heterocyclic and

-14-

most preferably comprises an oxygen or nitrogen atom in the ring. Preferably, the additive comprises an ester and/or an amide linkage internal to the ring of a cyclic chemical group.

5        Preferably, a ring-containing additive comprises at least one five member cyclic chemical group and/or one six member cyclic chemical group and/or one seven member cyclic chemical group in its molecular structure. More preferably, the ring-containing additive comprises at least one seven  
10 member cyclic chemical group in its molecular structure.

Although not wishing to be bound by theory, it is believed that when guest molecules, such as those in natural gases, dissolve in water and form clathrate hydrates, that water molecules cluster around the guest  
15 molecule, in a labile, non-permanent structure which closely resembles the  $5^{12}$  cavity. Two or more of these water clusters have been shown to share either vertices or faces, in the beginning of hydrate crystallization.

It is therefore possible to prevent clathrate hydrates  
20 from plugging, or otherwise impeding the flow of fluids by using a kinetic growth inhibitor to block small fluid-like species from becoming larger crystalline species.

One method of inhibition according to the process of the present invention, called kinetic inhibition, allows  
25 the system to exist in the hydrate thermodynamic stability region, but small clathrate hydrate masses are hindered from agglomerating with one another and/or from growing to form larger masses by means of small quantities of new

-15-

chemical treatments. It is believed that seven member cyclic chemical structures are particularly useful because they interact with one more of the pentagonal and/or hexagonal faces of a cavity, thereby preventing those faces 5 from participating in the formation of a larger clathrate hydrate mass.

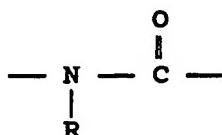
Preferably, the additive is a polymer of molecular weight greater than about 3,000, more preferably of molecular weight greater than about 10,000, still more 10 preferably of a molecular weight greater than about 20,000, and most preferably of molecular weight greater than about 40,000. As discussed below, some preferred polymers have molecular weights of one million or more. As used herein, polymer refers to homopolymers and copolymers. As used 15 herein, copolymer refers to a polymer made from any number of different monomers in excess of one.

One preferred class of ring-containing additives are those comprising one or more five, six and/or seven member cyclic chemical groups wherein at least one cyclic chemical 20 group comprises an internal ester or an internal amide. Examples of cyclic groups comprising internal amides include, for example, lactams, including those with substituents. Examples of cyclic groupings comprising internal esters include lactones and substituted lactones. 25 Additives comprising cyclic chemical groups representative of, or derived from, lactams or substituted lactams are particularly preferred. As used herein, a lactam includes

-16-

any organic ring having an amide linkage internal to the ring. Such an internal amide linkage has the formula

5



with the nitrogen atom and preferably also the carbon atom being in the ring. R can be hydrogen or another 10 constituent. Particularly preferred lactam rings include 2-pyrrolidone,  $\delta$ -valerolactam and/or  $\epsilon$ -caprolactam rings, which can be used in a substituted or unsubstituted form, and individually or in combination with one another.

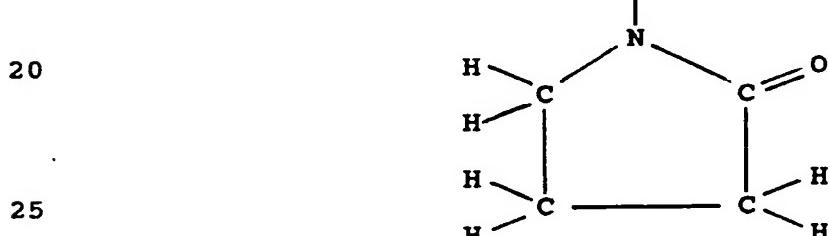
In one embodiment, the ring-containing additive 15 comprises a poly (N-vinyl lactam) homopolymer or copolymer. As used herein, poly(N-vinyl lactam) refers to polymers prepared using one or more monomers having a vinyl group substituted onto the nitrogen of a lactam ring. Preferred monomers are N-vinyl-2-pyrrolidone, N-vinyl- $\delta$ -valerolactam 20 and N-vinyl- $\epsilon$ -caprolactam, which can be individually polymerized to make homopolymers or can be copolymerized in any combination to prepare copolymers or can be copolymerized with other suitable non-lactam-containing monomers. Other ethylenically unsaturated groups, besides 25 the vinyl group, however, could be substituted onto the nitrogen of a lactam ring to provide other suitable monomers.

One ring-containing substance that has been found to be effective as an additive is poly(N-vinyl-2-pyrrolidone),

-17-

which comprises a plurality of five member cyclic groups extending from a polymer backbone. The five member cyclic groups comprise an internal amide characteristic of a lactam. Preferably, such poly(N-vinyl-2-pyrrolidone) is of 5 molecular weight greater than about 3,000, more preferably greater than about 10,000, still more preferably greater than about 20,000, and most preferably greater than about 40,000. Poly(N-vinyl-2-pyrrolidone) is a chemical with low toxicity. Therefore, it would not cause significant 10 environmental damage if accidentally released into the environment, such as might occur in case of a pipeline leak.

Poly(N-vinyl-2-pyrrolidone) is a polymer having a carbon backbone with the following five member cyclic group 15 having a pyrrolidone ring structure, referred to herein as Group I, which may be derived from 2-pyrrolidone, which is also called butyrolactam:

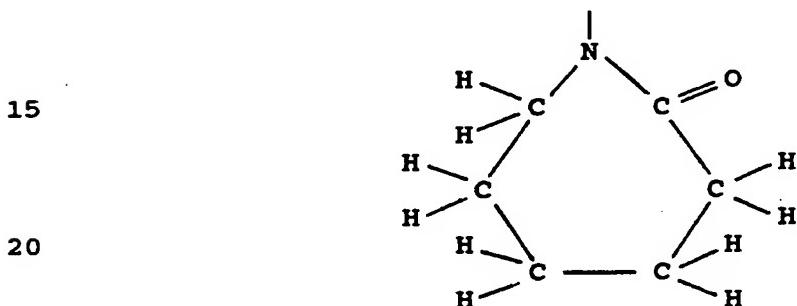


Other compounds having Group I could also be used as additives. Preferably, the additives are polymers having 30 a molecular weight greater than about 3,000, more preferably greater than about 10,000, still more preferably

-18-

greater than about 20,000 and most preferably greater than about 40,000. Group I could be incorporated into a polymer, for example, by homopolymerization of N-vinyl-2-pyrrolidone or by copolymerization with other monomers. Also, hydrogens 5 on the 2-pyrrolidone ring could be substituted with one or more organic groups.

In one embodiment, the ring-containing additive has a seven member cyclic group. One preferred seven member cyclic group is the following group having a caprolactam 10 ring structure, referred to herein as Group II, which may be derived from  $\epsilon$ -caprolactam:



Group II

The additive is preferably a polymer, more preferably having a molecular weight greater than about 3,000, more 25 preferably greater than about 10,000, still more preferably greater than about 20,000 and most preferably greater than about 40,000. Such a caprolactam group could, for example, extend from a polymer backbone, such as a polyvinyl 30 backbone. Group II could be incorporated into a polymer, for example, by homopolymerization of N-vinyl- $\epsilon$ -caprolactam or copolymerization with other monomers. Also, hydrogens

-19-

on the  $\epsilon$ -caprolactam ring could be substituted with one or more organic groups. The  $\epsilon$ -caprolactam ring structure has been found to be particularly effective for controlling clathrate hydrates and homopolymers and copolymers made 5 from N-vinyl- $\epsilon$ -caprolactam are particularly preferred ring-containing additives.

In one embodiment, the ring-containing additive comprises a plurality of different cyclic chemical groups. Preferably, the additive comprises at least two cyclic 10 chemical groups and more preferably, the additive comprises a first cyclic chemical group having a different number of atoms in its ring than a second cyclic chemical group. Even more preferably, the additive comprises a five member cyclic chemical group and a seven member cyclic chemical 15 group. Preferably at least one of the cyclic chemical groups comprises an internal amide and/or an internal ester and more preferably at least two different cyclic chemical groups comprise an internal amide and/or an internal ester. Preferably, the additive is a polymer with a molecular 20 weight greater than about 3,000, more preferably greater than about 10,000, still more preferably greater than about 20,000 and most preferably greater than about 40,000. The additive preferably is also at least partially soluble in water. In one preferred embodiment, the multiple cyclic 25 chemical groups are such that they do not form a part of the polymer backbone, but rather extend from the polymer backbone, such as would be the case for substituents grafted onto a polymer backbone. One such preferred

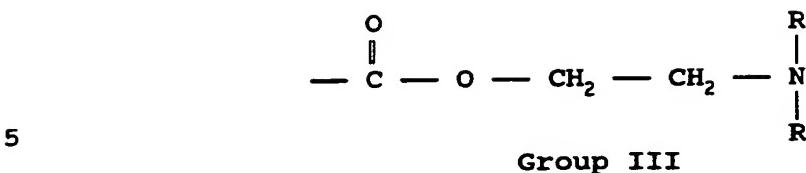
-20-

additive is a copolymer having both pyrrolidone and  $\epsilon$ -caprolactam rings, such as a copolymer between N-vinyl-2-pyrrolidone and N-vinyl- $\epsilon$ -caprolactam. Such a copolymer can be made from any ratio of the comonomers, but preferably is  
5 made from greater than about 25 weight percent N-vinyl- $\epsilon$ -caprolactam, more preferably from greater than about 50 weight percent N-vinyl- $\epsilon$ -caprolactam, still more preferably from greater than 65 weight percent N-vinyl- $\epsilon$ -caprolactam and most preferably greater than about 75 weight percent N-  
10 vinyl- $\epsilon$ -caprolactam.

In one embodiment, the ring-containing additive has, in addition to multiple cyclic chemical groups which are not a part of the polymer backbone, at least one noncyclic chemical group also extends from the polymer backbone. Such  
15 a noncyclic chemical group can comprise either a normal or a branched chain structure. Preferably, the noncyclic chemical group comprises at least one polar atom such as oxygen, nitrogen, sulfur or phosphorus, more preferably nitrogen and/or oxygen. One preferred noncyclic chemical  
20 group comprises an amino or substituted amino group.

In one embodiment, the ring-containing additive comprises a five member cyclic chemical group, a seven member cyclic chemical group, and a noncyclic chemical group. Preferably, all three of these chemical groups form  
25 or are part of substituents extending from a polymer backbone. One chemical that has been found to be particularly useful comprises Group I, Group II and the following noncyclic group, referred to herein as Group III:

-21-



Where each R is independently hydrogen or an organic constituent. Preferably, Group III is made from polymerizing an N,N-disubstituted ethyl amino methacrylate monomer and more preferably from polymerizing 2-[dimethylamino]ethyl methacrylate, in which both of the R's in Group III are methyl groups. The polymer can be any polymer with these three chemical groups, and may be, for example, block, random, or graft copolymers. Group III could be incorporated into a polymer, for example, by copolymerization of 2-[dimethylamino]ethyl methacrylate with other appropriate monomers to form a copolymer having all of Groups I, II and III. Preferably, the polymer has a molecular weight greater than about 3,000, more preferably greater than about 10,000, still more preferably greater than about 20,000 and most preferably greater than about 40,000. Alternatively, an additive may have Group III and only one of Group I and Group II.

One specific example of a compound having all of Groups I, II and III is that sold under the name "Gaffix VC-713" by International Specialty Products which currently has a business address of 1361 Alps Road, Wayne, New Jersey. Gaffix VC-713 is a copolymer prepared from three monomers, which is often referred to as a terpolymer.

-22-

Those three monomers are N-vinyl-2-pyrrolidone, N-vinyl- $\epsilon$ -caprolactam and 2-[dimethylamino]ethyl methacrylate.

Another preferred ring-containing additive is hydroxyethylcellulose, which comprises six membered cyclic 5 chemical groups. Any of the additives discussed herein, can be used together in any ratios.

In one aspect, the present invention provides a method for increasing the effectiveness of ring-containing additives discussed previously, and especially ring-10 containing additives that comprise one or more lactam rings. With increased effectiveness, less additive can be used and the cost of controlling clathrate hydrates, is correspondingly reduced.

One apparent problem with polymeric additives having 15 organic rings, as described, is that the polymers appear to have a tendency to associate with one another when dissolved in water. Polymer molecules do not appear to be individually well dispersed in the solution. It is believed that this lack of good dispersion reduces the effectiveness 20 of the ring-containing polymers because it is difficult for some functional groups on the polymer to interact with clathrate hydrate masses in such a way as to inhibit the growth of those masses.

Another apparent problem is that individual polymer 25 molecules appear to have a tendency to exist in aqueous solution in a compact conformation. As used herein, conformation refers to the shape or arrangement in three-dimensional space that an organic molecule assumes.

-23-

Allowing polymers to assume a less compacted, and more extended and open, conformation results in more effective utilization of the polymers for controlling clathrate hydrate problems. For example, the caprolactam groups on 5 a poly(N-vinyl- $\epsilon$ -caprolactam) appear to have a tendency to associate with one another in an aqueous solution, thereby keeping the polymer in a compact conformation and preventing some of the  $\epsilon$ -caprolactam rings from effectively inhibiting the growth of clathrate hydrate masses.

10        Certain modifications can be made to chemical additives used with the present invention to improve the effectiveness of those additives. Not to be bound by theory, it is believed that the improvement in effectiveness is due to reduced association between polymer 15 molecules and/or to individual polymer molecules attaining a more extended, and less compact, conformation in an aqueous solution.

In one embodiment, functional ring constituents on polymers are sterically hindered to prevent their 20 association. For example, the compound Gaffix VC-713, as previously described, comprises both pyrrolidone rings and caprolactam rings. Gaffix VC-713 is made from about 65 weight percent N-vinyl- $\epsilon$ -caprolactam, 25 weight percent N-vinyl-2-pyrrolidone, and 10 weight percent of 25 [dimethylamino]ethyl methacrylate. Gaffix VC-713, however, performs as effectively in controlling clathrate hydrate problems as does an N-vinyl- $\epsilon$ -caprolactam homopolymer, which comprises a larger number of the N-vinyl- $\epsilon$ -

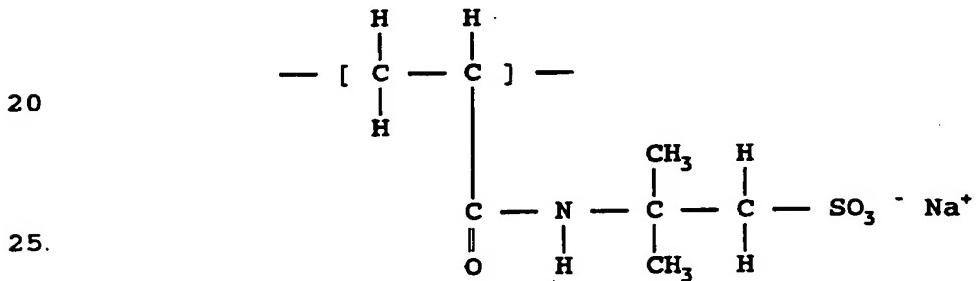
-24-

caprolactam units per unit weight than does the Gaffix VC-713 polymer. Consequently, it may be that the presence of the pyrrolidone rings in Gaffix VC-713 provides steric hinderance to association of the caprolactam rings. This  
5 may be due to the relative greater attraction of water molecules to the pyrrolidone rings relative to the caprolactam rings. This steric hinderance may have the effect of extending the molecule more in the Gaffix VC-713 than is the case for the N-vinyl- $\epsilon$ -caprolactam homopolymer.  
10 Other nonionic groups could also be used to provide steric hinderance between organic ring constituents on a polymer.

Ionic groups can also be used to provide steric hinderance. The use of ionic groups also provides the added benefit of charge repulsion, which should tend to  
15 further disassociate the polymer molecules from one another and extend the individual polymer molecules in solution. Anionic groups are preferred. Such anionic groups include sulfonates, sulfinites, sulfates, phosphonates, phosphinates, phosphates, and carboxylates. Sulfonates are  
20 generally preferred. As used herein, sulfonate, sulfinate, sulfate, phosphonate, phosphinate, phosphate and carboxylate each include the respective acids, although the use of such acids is not preferred. Preferably, the ionic groups are in a salt form and more preferably in salt form  
25 with a cation of a Group IA metal or with an ammonium cation. Preferably, the ionic groups are present in the form of a polyelectrolyte.

-25-

In one embodiment, a polyelectrolyte can be mixed with one of the ring-containing hydrate control polymers as previously described. Preferably, however, the ionic groups and the ring structures useful for clathrate hydrate control are combined in a single polymer. For example, a copolymer from monomers comprising N-vinyl-pyrrolidone and sodium 2-acrylamido-2-methyl-1-propane sulfonate could be used. Such polymers that combine ring structures and ionic groups may be of very high molecular weight. The molecular weight of such polymers may be on the order of one million or more. One such high molecular weight polymer is a copolymer made from the three monomers N-vinyl-2-pyrrolidone, 2-acrylamido-2-methyl-1-propane sulfonate, and acrylamide. Polymerization of sodium 2-acrylamido-2-methyl-1-propane sulfonate provides in the copolymer the repeating unit:



This copolymer is manufactured by Phillips Petroleum Company and sold under the name HE-300. Addition of the acrylamide monomer has the effect of producing a higher molecular weight polymer. Methacrylamide could also be used as a comonomer as could any ethylenically unsaturated

-26-

compound that is copolymerizable by a free radical technique.

One preferred copolymer comprises both an organic ring having nitrogen as a hetero atom, such as a lactam ring which contains an amide internal to the ring, and a noncyclic amide, being an amide that does not form a part of an organic ring. The noncyclic amide may be unsubstituted. Preferably, however, the noncyclic amide is N-substituted, as discussed later. The HE-300 compound is one example of a copolymer having both an amide internal to a ring and a noncyclic amide. As with HE-300, the internal amide and the noncyclic amide are preferably part of pendent constituents that are attached to and extend from a polymer backbone, such as a polyvinyl backbone or other backbone representative of polymerizing ethylenically unsaturated monomers. Acrylamide monomers are preferred for incorporating the noncyclic amide. The N-substituted acrylamide monomers, discussed later, are especially preferred.

In another aspect, the present invention provides new chemical additives useful in preventing problems with clathrate hydrates. The chemicals are polymers comprising a polymer backbone having at least two different constituents pendent from the backbone. A first constituent comprises a seven member organic ring. A second constituent comprises an ionic group. Preferably, the ionic group is an anionic group.

-27-

Preferably, the seven member ring comprises an ester and/or an amide linkage internal to the ring. Preferably, the seven member ring is an  $\epsilon$ -caprolactam ring.

The anionic groups are preferably sulfonates, 5 sulfonates, sulfates, phosphonates, phosphinates, phosphates and/or carboxylates. Sulfonates are more preferred. The ionic groups are preferably associated as salts with either Group IA metal cations or an ammonium cation.

10 The polymers can be prepared from any ethylenically unsaturated monomers having seven member ring constituents and ionic group constituents. Preferably, the monomers are ethylenically monounsaturated to reduce possible crosslinking. One preferred polymer can be made by 15 copolymerizing N-vinyl- $\epsilon$ -caprolactam with sodium 2-acrylamido-2-methyl-1-propane sulfonate. Also, other ethylenically unsaturated monomers can be used, such as acrylamide and methacrylamide monomers, which may be substituted or unsubstituted. A copolymer from the three 20 monomers of N-vinyl- $\epsilon$ -caprolactam, sodium 2-acrylamido-2-methyl-1-propane sulfonate, and acrylamide is one preferred polymer additive.

Several methods for initiating free radicals for 25 polymerizing ethylenically unsaturated monomers are known in the art. The polymers of the present invention can be prepared by these known free radical initiation polymerization methods.

-28-

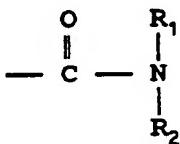
In addition to the ring-containing additives just discussed, some additives have been identified that do not require the presence of an organic ring. One such group of additives that has been found useful for controlling 5 clathrate hydrate problems includes alkoxy compounds. As used herein, alkoxy compounds include any compounds having one or more alkoxy groups, and preferably comprising one or more ethoxy and/or propoxy groups. Such alkoxy compounds may comprise a compound which has been alkoxylated through 10 substitution to introduce one or more alkoxy groups. Alkoxy compounds also include polyethers, and particularly polyethers comprising repeating units characteristic of ring opening polymerization of ethylene oxide and/or propylene oxide and/or their derivatives.

15 One preferred alkoxy additive is a polymer having first repeating units characteristic of ring opening polymerization of ethylene oxide and second repeating units characteristic of ring opening polymerization of a propylene oxide. In one embodiment, the alkoxy compound 20 comprises one or more polyether blocks of ethoxy repeating units, characteristic of ring opening polymerization of ethylene oxide. In another embodiment, the alkoxy compound comprises one or more polyether blocks of propoxy repeating units. In one preferred embodiment, the alkoxy compound 25 comprises one or more ethoxy polyether blocks and one or more propoxy polyether blocks. More preferably, the alkoxy compound is a block copolymer. In one embodiment, such a block copolymer is of a formula EO-PO-EO, with EO

-29-

representing an ethoxy block and PO representing a propoxy block. In another embodiment, the block copolymers have the formula PO-EO-PO. Preferably, ethoxy blocks comprise at least 60 weight percent of these block copolymers, and 5 more preferably greater than 70 weight percent.

One group of additives that has been found to be particularly effective for controlling clathrate hydrate problems, and which does not require the presence of an organic ring, comprises a polymer having a backbone with a pendent constituent attached to and extending from the backbone which comprises a noncyclic N-substituted amide. By noncyclic, it is meant that none of the amide group forms part of an organic ring. The polymer may be a homopolymer or a copolymer made from two or more monomers. 10 15 Preferably, the pendent constituent comprises the group



where one or both of  $\text{R}_1$  and  $\text{R}_2$  is an organic group that is not hydrogen. The pendent constituent having the noncyclic N-substituted amide could be part of any repeating unit representative of polymerizing an ethylenically unsaturated monomer polymerizable by free radical polymerization. 20 25 Preferably, however, the polymer has at least some repeating units representative of polymerizing an N-substituted acrylamide. These noncyclic amide-containing additives can be used alone or in combination with other 30 additives, as discussed below.

-30-

The substituent attached to the nitrogen of the noncyclic amide may be any radical other than hydrogen. Therefore, the nitrogen of the noncyclic amide will have, at most, one hydrogen attached to it. Organic groups having  
5 one to four carbon atoms are preferred substituents. Alkyl substituents are more preferred. Furthermore, it has been found that certain sizes of substituents provide unexpectedly superior results. Therefore, it is particularly preferred that at least one substituent  
10 comprises a methyl, ethyl or propyl group.

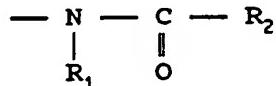
The noncyclic amide may be an N-monosubstituted amide, with the single substituent preferably being a C<sub>2</sub> or C<sub>3</sub> organic group. An N-ethyl amide is particularly preferred. Alternatively, the noncyclic amide can be an N,N-disubstituted amide, and preferably with at least one methyl substituent. An N,N-dimethyl amide is particularly preferred. Not to be bound by theory, it is possible that certain substituent(s) are of a size that is conducive to the formation around the substituent of a pseudo-hydrate or  
15 other ordered arrangement of water molecules that ties up water molecules and prevents them from participating in clathrate hydrate formation. Substituents that are too large or too small would not be effective for forming such an ordered arrangement of water molecules. One example of  
20 such an additive is a polymer having at least some repeating units representative of polymerizing N-methyl-N-vinylacetamide. One particularly effective additive  
25 comprises at least some repeating units representative of

-31-

polymerizing N-ethyl acrylamide. Another particularly effective polymer is one having at least some repeating units representative of polymerizing N,N-dimethylacrylamide. Another particularly effective polymer 5 is one having at least some repeating units representative of polymerizing N-isopropyl acrylamide, such as poly(N-isopropyl acrylamide).

Another group of additives which does not require the presence of an organic ring comprises a polymer having a backbone with a pendent constituent which comprises a noncyclic amide in which the nitrogen atom of the amide occupies a position within the pendent constituent that is closer to the backbone than is the position occupied by the carbonyl carbon of the amide. The carbonyl carbon is at a 10 position that is more removed from the backbone than the nitrogen. The pendent constituent, therefore, comprises 15 the group

20



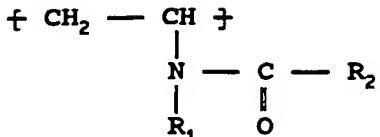
where R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or an organic group. Preferably, at least one of R<sub>1</sub> and R<sub>2</sub> is an alkyl group. C<sub>1</sub>-C<sub>4</sub> alkyl groups are especially preferred. The polymer can be a homopolymer or a copolymer.

25

Preferably, the nitrogen of the amide is attached to the backbone. One such additive, having the nitrogen of the amide attached to the backbone, is a polymer having at least some of the following repeating unit, which is representative of polymerizing an N-vinyl alkyl amide:

-32-

5



where  $\text{R}_1$  and  $\text{R}_2$  are each independently an alkyl or hydrogen. For example, if the additive has a repeating unit representative of polymerizing N-methyl-N-vinylacetamide, then both  $\text{R}_1$  and  $\text{R}_2$  are methyl. If the additive has a 10 repeating unit representative of polymerizing N-vinylacetamide, then  $\text{R}_1$  is H and  $\text{R}_2$  is  $\text{CH}_3$ . If the additive has a repeating unit representative of polymerizing N-vinylformamide, then both  $\text{R}_1$  and  $\text{R}_2$  are H.

In one embodiment, an additive could be a copolymer 15 comprising a first repeating unit having an organic ring and a second repeating unit having the pendent constituent with the noncyclic amide. For example, an N-vinyl lactam could be copolymerized with an N-vinyl alkyl amide.

Also, it should be noted that a common characteristic 20 of many of the polymer additives having a noncyclic amide that are particularly preferred is that there is a relatively small organic group or groups attached to the nitrogen and/or to the carbonyl carbon of the noncyclic amide. As mentioned previously, but not to be bound by theory, it appears that groups of a certain size may be 25 conducive to formation around the group of a pseudo-hydrate or other ordered arrangement of water molecules that ties up water molecules and prevents them from participating in clathrate hydrate formation. Preferred groups have from 30 one to four carbon atoms and are also preferably alkyl

-33-

groups. Methyl, ethyl and propyl groups are particularly preferred. Specific examples of polymer repeating units having one or more such relatively small organic groups attached to the nitrogen and/or the carbonyl carbon atom of  
5 a noncyclic amide include those repeating units representative of polymerizing 2-methyl-2-oxazoline, 2-ethyl-2-oxazoline, N-ethyl acrylamide, N-isopropyl acrylamide, N,N-dimethylacrylamide, N-methyl-N-vinylacetamide or N-vinylacetamide. In each of these  
10 representative repeating units, the relatively small organic group or groups are attached to a nitrogen atom and/or a carbonyl atom that are part of a pendent constituent that is attached to and extends from a polymer backbone. In the case of polymers having oxazoline-based  
15 repeating units, the carbonyl carbon is a part of the pendent constituent. For acrylamide-based repeating units and N-vinyl alkyl amide-based repeating units, both the nitrogen and the carbonyl carbon are part of the pendent constituent.

20 In a further aspect, the present invention provides for the use of one or more of the previously described clathrate hydrate control additives as primary additives in combination with one or more other substances as a secondary additive. It has been found that many of the  
25 primary additives perform satisfactorily in smaller quantities when those additives are mixed with certain secondary additives. Also, many of the secondary additives are less costly and can, therefore, provide significant

-34-

cost savings. Use of secondary additives is particularly useful for primary additives having one or more lactam rings. Also, any of the previously described additives can be used together, in any combination, with one additive 5 acting as a primary additive and a second additive acting as a secondary additive.

In one embodiment, the primary additive comprises an organic ring, preferably having an amide linkage internal to the ring, such as those additives previously described. 10 One or more primary additive is mixed with one or more alcohols, as a secondary additive, such that the primary additive and the alcohol are substantially simultaneously contacted with a fluid that is susceptible to having clathrate hydrate problems. Preferably, the primary 15 additive and the alcohol are mixed prior to contacting the two additives with the fluid. In another embodiment, the primary additive could be any of the polymers described herein having a noncyclic amide.

One benefit of using alcohols is that alcohols tend to 20 suppress the hydrate formation temperature. It appears, however, that alcohols provide an additional benefit of improving the effectiveness of the primary additives to prevent the growth and/or agglomeration of clathrate hydrate masses once they have formed. This additional 25 benefit may be due to reducing association between primary additive molecules and/or by promoting a greater extension of individual molecules of the primary additive in solution.

-35-

The alcohol is preferably soluble in water. More preferably, the alcohol is a C<sub>1</sub>-C<sub>5</sub> monohydric or polyhydric alcohol. The most preferred alcohols are methanol, ethanol and ethylene glycol, with methanol being particularly  
5 preferred.

The alcohol can be used with primary additives in any ratio. The alcohol is preferably added in an amount that is greater than about 1 weight percent relative to water in the fluid, more preferably greater about 2 weight percent,  
10 and most preferably from about 2 weight to about 20 weight percent. The primary additive is preferably added in an amount of from about 0.1 weight percent to about 1.0 weight percent relative to water.

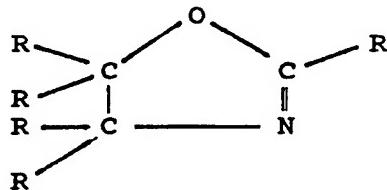
In another embodiment, the secondary additive  
15 comprises a nitrogen-based linkage. Preferably, the nitrogen-based linkage is an amide linkage. Such an amide linkage may be internal to a ring, such as in a lactam ring. For example, poly(N-vinyl- $\epsilon$ -caprolactam) can be mixed with HE-300, either of which can be the primary additive  
20 with the other being the secondary additive. Such a mixture has been found to be more effective than either of the two additives used separately. Also, mixtures of an N-vinyl- $\epsilon$ -caprolactam/N-vinyl-2-pyrrolidone copolymer and HE-300 are also useful for controlling clathrate hydrates. Use of a  
25 copolymer made from greater than about 75 weight percent N-vinyl- $\epsilon$ -caprolactam is preferred. One mixture that has been shown to be particularly effective is a mixture, relative to water, of approximately 0.25 weight percent HE-300 and

-36-

0.25 weight percent of a 75/25 by weight copolymer of N-vinyl- $\epsilon$ -caprolactam/N-vinyl-2-pyrrolidone. Preferably, however, the mixture should contain at least about 0.50 weight percent of the 75/25 copolymer with at least about 5 0.25 weight percent HE-300. Such a mixture is effective at preventing problems with gas hydrates at a temperature of 39.2°C and a pressure of 1500 psi for a significant period of time. Another useful combination is to mix poly(N-vinyl-2-pyrrolidone) and poly(N-vinyl- $\epsilon$ -caprolactam), which 10 appears to provide enhanced performance relative to use of the polymers individually.

The amide linkage of the secondary additive need not, however, be an amide linkage internal to a ring. For example, the added substance may comprise materials such as 15 polypeptides. One preferred additive is a polymer having at least some repeating units characteristic of polymerizing an oxazoline monomer. Preferred oxazoline monomers are 2-oxazolines, which have the chemical formula

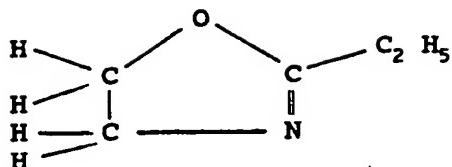
20



25 where each R can be independently hydrogen or an organic substituent. A preferred 2-oxazoline monomer is 2-ethyl-2-oxazoline which has the chemical formula

-37-

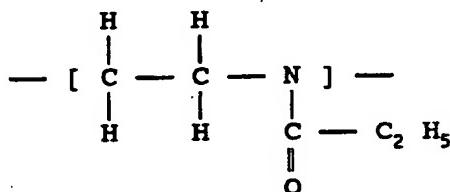
5



Polymerization of 2-ethyl-2-oxazoline gives a repeating unit of the following formula

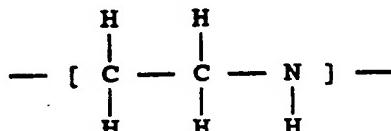
10

15



Another preferred 2-oxazoline monomer is 2-methyl-2-oxazoline. In one embodiment, at least a portion of the oxazoline repeating units are hydrolyzed to give at least some repeating units of

20



25

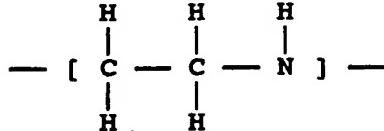
The oxazoline-based polymers can be used to replace at least a part of the primary additives. For example, a mixture, relative to water, of 0.25 weight percent poly(2-ethyl-2-oxazoline) and 0.25 weight percent poly( $N$ -vinyl- $\epsilon$ -caprolactam) should be effective to prevent gas hydrate problems at a pressure of 1000 psi and 39.2°C for a significant time.

Useful secondary additives can also be prepared from polymerization of ethylene imine by a ring opening

-38-

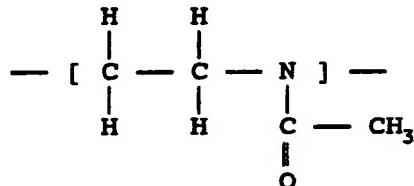
polymerization of the ethylene imine to give the following repeating units

5



Additionally, the poly(ethyleneimine) can be treated with a substance to substitute at least some of the hydrogens of 10 the poly(ethyleneimine). Treatment with acetyl chloride, for example, will give repeating units of the formula

15



These repeating units are the same as those obtained from 20 polymerizing 2-methyl-2-oxazoline. The number of those repeating units in the polymer, however, will vary depending upon the number of substitutions made on the nitrogen sites.

Preferably, at least some of the nitrogen-based 25 linkages of the secondary additive comprise a tertiary amide. For example, the internal amide linkage of an N-vinyl caprolactam polymer and a polymer from 2-ethyl-2-oxazoline both have tertiary amides. A poly(ethyleneimine) treated with acetyl chloride will have some tertiary 30 amides, the number depending upon the number of substituted sites.

-39-

One combination of primary and secondary additives that has been found to be particularly effective is when the primary additive comprises a heterocyclic organic ring having nitrogen as a hetero atom and the secondary additive 5 comprises a noncyclic amide, that is, an amide that is external to an organic ring. It is preferred that the primary additive have an amide internal to the ring, as in the lactam-containing additives described previously, and that both the primary and secondary additives are polymers. 10 Preferably, the noncyclic amide is part of a pendent constituent that is attached to and extends from a polymer backbone. In one embodiment, the noncyclic amide is part of a pendent constituent that is attached to and extends from a polymer backbone and in which the nitrogen of the 15 noncyclic amide occupies a position that is closer to the backbone than is the position occupied by the carbonyl carbon of the noncyclic amide, such as would be the case for a polymer having at least some of a repeating unit representative of polymerizing an N-vinyl alkyl amide. In 20 one preferred embodiment, the noncyclic amide is N-monosubstituted or N,N-disubstituted, as previously described. In yet another embodiment, the noncyclic amide is in a polymer having at least some repeating units representative of polymerizing an oxazoline monomer, as 25 previously discussed. Some examples of preferred combinations of additives include mixtures of at least one of Gaffix VC-713, poly N-vinyl- $\epsilon$ -caprolactam and a copolymer of N-vinyl- $\epsilon$ -caprolactam and N-vinyl-2-

-40-

pyrrolidone with at least one of poly(N,N-dimethylacrylamide), poly(N-ethyl acrylamide), poly(N-isopropyl acrylamide), poly(N-methyl-N-vinylacetamide) and poly(2-ethyl-2-oxazoline).

Combining a primary additive having a heterocyclic organic ring with nitrogen as a hetero atom and a secondary additive having a noncyclic amide appears to provide a synergistic effect. Although some of the additives used alone have been found to be effective at a pressure of about 1000 psi and a temperature of 39.2°F, none of the additives alone have been found to be effective at significantly higher pressures. In one embodiment of the present invention, however, clathrate hydrate masses in a fluid are subjected to a temperature of less than about 45°C and a pressure of higher than about 1500 psi without formation of clathrate hydrate masses that are large enough to block or seriously impede fluid flow. Preferably, the fluid is subjected to a temperature of lower than about 40°F, which is often encountered during subsea pipeline transportation, especially in the North Sea. Preferably, the fluid is subjected to a pressure of higher than about 1900 psi and more preferably higher than about 2000 psi. The ability to operate at these higher pressures permits transportation of a significantly larger volume of fluid through a pipeline under conditions at which the fluid is susceptible to formation of a clathrate hydrate. This is particularly advantageous in places like the North Sea where pipeline capacity from offshore petroleum platforms

-41-

is often lower than the capacity of the offshore petroleum production facility to deliver produced fluids.

The fluid system to which hydrate control additives can be added comprises any fluid or fluids comprising water and guest molecules, which water and guest molecules together can form clathrate hydrates. The fluid system may comprise any combination of one or more gaseous phase, aqueous liquid phase, and organic liquid phase, and in any proportions. Typically, the fluid system will comprise at least two fluid phases, a gaseous phase, which comprises guest molecules, and an aqueous liquid phase. Typically, a suitable fluid system comprising an organic liquid phase also comprises both a gaseous phase and an aqueous liquid phase.

The present invention is particularly useful in fluid systems comprising a continuous aqueous liquid phase. A continuous aqueous liquid phase is, for example, an aqueous phase that is not dispersed as small, emulsified droplets throughout a continuous organic phase, as would be the case in a water-in-oil type emulsion. Therefore, the present invention is particularly useful, for example, when the fluid system comprises a gaseous phase and an aqueous liquid phase in the absence of an organic liquid phase, or at least in the absence of an organic liquid phase of significant volumetric proportion relative to the aqueous liquid phase. It has been surprisingly discovered that, according to the present invention, clathrate hydrate masses in such a fluid system, containing a continuous

-42-

aqueous liquid phase will nonetheless disperse in the fluid system, and in particular will disperse in the continuous aqueous liquid phase, and will not agglomerate to form a mass large enough to impede the flow of a fluid stream comprising the dispersed clathrate hydrate masses. This is particularly surprising because, in the absence of a substantial organic liquid phase, the aqueous liquid phase cannot be emulsified and dispersed throughout the organic phase to maintain dispersion of clathrate hydrates forming in small, dispersed aqueous droplets.

With the present invention, it is not necessary to disperse an aqueous liquid phase, such as throughout an organic liquid phase, to prevent agglomeration of clathrate hydrate masses. With the present invention, even in a fluid system that contains a shortage of available water relative to available guest molecules for the formation of clathrate hydrates, not all of the water will participate with guest molecules to form clathrate hydrates. Rather, free water will typically remain in an aqueous liquid phase, which will have clathrate hydrate masses dispersed therein.

Based on the foregoing, it will be recognized that the present invention has wide applicability to fluid systems of varying relative proportions of gaseous, aqueous liquid, and organic liquid phases. The present invention, for example, will disperse clathrate hydrates in an aqueous phase, whether such aqueous phase is in a gas/aqueous liquid system or in a gas/aqueous liquid/organic liquid system. Also, in a gas/aqueous liquid/organic liquid

-43-

system, it is not necessary that the organic liquid phase predominates over the aqueous liquid phase because it is not necessary to disperse the aqueous phase as small droplets in an emulsified form.

- 5        In one embodiment, the fluid comprises a saline aqueous liquid. The ring-containing and other clathrate control additives useful with the present invention have, surprisingly, been found to be effective for controlling clathrate hydrate problems in such saline aqueous liquids.
- 10      Lactam-containing compounds, and preferably polymers comprising one or more lactam rings, have been found to be particularly effective in treating such saline solutions. In one embodiment, the aqueous liquid comprises greater than about 1 weight percent dissolved salt. In another
- 15      embodiment the aqueous liquid comprises greater than about 2 weight percent of dissolved salt. In a further embodiment, the aqueous liquid comprises greater than about 3 weight percent of dissolved salt. In a still further embodiment, the aqueous liquid comprises greater than about
- 20      3.5 weight percent dissolved salt, such as might be found in sea water. For example, a mixture of 0.25 weight percent of a 75/25 copolymer of N-vinyl- $\epsilon$ -caprolactam/N-vinyl-2-pyrrolidone and 0.25 weight percent of HE-300, relative to water, has been found effective in laboratory experiments
- 25      for controlling clathrate hydrates for a significant time at a pressure of 1,500 psi, a temperature of 39.2°F, and with a water phase comprising approximately 3.5 weight percent of dissolved salt. These additives, when used

-44-

alone, have not been found to be effective in the laboratory at pressures higher than 1000 psi at 39.2°F.

Additionally, increasing the salt concentration up to 3.5 weight percent relative to water significantly enhances 5 the hydrate control effectiveness of additives comprising a 5 member ring. Preferably, the additive comprises a polymer having a plurality of pyrrolidone rings, such as, for example, a homopolymer or copolymer of N-vinyl-pyrrolidone. A copolymer of N-vinyl-2-pyrrolidone 10 preferably comprises an  $\epsilon$ -caprolactam ring. A preferred copolymer is one made from N-vinyl-2-pyrrolidone and N-vinyl- $\epsilon$ -caprolactam, including the Gaffix VC-713 copolymer.

Contacting an additive with clathrate hydrates in a fluid system, according to the present invention, can be 15 accomplished using any suitable contacting means. For example, such contacting can be effected by mixing an additive into the fluid system, such as into a flowing fluid stream. For example, an additive could be injected into a downhole location in a producing well to control 20 clathrate hydrates in fluids being produced through that well. Likewise, an additive could, for example, be injected into the produced fluid stream at a wellhead location, or even into piping extending through a riser, through which produced fluids are transported in offshore producing 25 operations from the ocean floor to the offshore producing facility located at or above the surface of the water. Also, an additive could be injected into a fluid stream prior to transporting that fluid stream, such as by

-45-

injecting an additive into the fluid stream which is then transported, such as via subsea pipeline from an offshore producing location to an onshore processing facility.

Additives useful according to the present invention, 5 can be normally solid, normally liquid, or normally gaseous. If such an additive is normally solid, such as is the case with many polymers, including poly(N-vinyl-2-pyrrolidone), such solid additive is preferably dissolved into a carrier liquid, so that the additive can then be 10 injected into the fluid system in liquid form. For example, poly(N-vinyl-2-pyrrolidone), poly(N-vinyl- $\epsilon$ -caprolactam), copolymers of the two, Gaffix VC-713, HE-300, hydroxyethylcellulose, poly(N-ethyl acrylamide), poly(N-isopropyl acrylamide), poly(N,N-dimethylacrylamide) and 15 other additives, can be dissolved in methanol, and the methanol solution can then be injected directly into a flowing fluid stream to effect a desired contacting of the additive with clathrate hydrate masses that may form in the fluid stream during transportation, such as through a 20 pipeline. The carrier liquid should preferably be soluble in water. Water, however, is generally not preferred as a carrier liquid because of the tendency of such water to promote additional clathrate hydrate formation in the fluid system.

25 Preferably, an additive is mixed with the fluid system prior to the formation of clathrate hydrates in that fluid system. The additive would then be present in the fluid

-46-

system to contact clathrate hydrate masses as they first form.

Mixing of an additive into the fluid system, or contacting of an additive already in the fluid system with 5 clathrate hydrate masses, may be aided by mechanical means, as are well known in the art, such as, for example, by using conveniently located static, in-line mixers on a pipeline. In most pipeline transportation applications, however, sufficient mixing and contacting will occur due to 10 the turbulent nature of the fluid flow and mechanical mixing aids will not be required.

It will be recognized that the amount of primary additive required to be added to any particular fluid system will depend upon the composition of that system and 15 the conditions of temperature and pressure to which the fluid system will be subjected. Generally, however, such additive will be added in an amount that results in from about 0.01 weight percent to be about 10 weight percent, preferably from about 0.1 weight percent to about 5 weight 20 percent and more preferably from about 0.2% to about 0.5%, by weight, of additive relative to free water in a fluid system.

The following examples are provided for the purpose of illustrating the present invention and are not intended to 25 limit the scope of the invention in any way.

-47-

Example 1

This example is provided for comparison, and illustrates the formation of clathrate hydrates in an aqueous solution and growth of those clathrate hydrates 5 into masses of sufficient size to form a clathrate hydrate plug in a fluid system.

A 15 ml test tube is filled with an aqueous solution containing 3.5 weight percent sodium chloride, relative to water, and 20 weight percent of tetrahydrofuran, also 10 relative to water. Tetrahydrofuran is a compound capable of forming a clathrate hydrate. A stainless steel ball having an outside diameter of 0.20 inch is inserted into the test tube so that the ball can roll freely along the tube length. The test tube is sealed and placed in a water bath 15 containing ice that is at a temperature of 0°C. A mechanical device rotates the test tube continuously end-over-end about the center point of the length of the test tube. The stainless steel ball rolls from one end of the test tube to the other during each rotation of the test 20 tube. The test tube is visually observed while rotating in such a fashion.

The solution becomes cloudy, indicating the initiation of a clathrate hydrate phase within the tube, after about twelve minutes of rotating in the water bath. After 25 approximately thirty minutes of rotating in the water bath, the ball completely stops rolling in the test tube, indicating that clathrate hydrates have formed a plug within the test tube.

-48-

Example 2

This example illustrates the use of an additive to prevent aggregation of clathrate hydrates in an aqueous solution to form a clathrate hydrate plug.

5       The experimental procedure of Example 1 is repeated, except that poly(N-vinyl-2-pyrrolidone) is added to the aqueous solution in an amount of 0.5 percent by weight, relative to water. The solution in the test tube becomes cloudy after approximately 45 minutes of rotating in the  
10      water bath. After 6 hours of rotating in the water bath, the ball is still rolling. Normally, even if this experiment is continued after 6 hours, the ball continues to roll in the test tube even after a period of 24 hours.  
15      Therefore, the additive prevents the formation of a clathrate hydrate plug in the test tube over what is be a commercially significant period of time.

Example 3

This example illustrates the use of Gaffix VC-713, as previously described, to control the formation and/or  
20.     agglomeration of clathrate hydrates.

The experimental procedure of Example 1 is repeated, except that Gaffix VC-713 is added to the aqueous solution in an amount of 0.5 percent by weight, relative to water. After eight hours of rotating in the water bath, the  
25     solution in the test tube shows no signs of hydrate formation.

-49-

Example 4

This example demonstrates the surprising effect of using a primary additive having a lactam ring and a secondary additive having a noncyclic amide.

5        Various polymer additives are tested in a 300 cubic centimeter, high pressure, stirred autoclave. During each test, gas is fed into the autoclave from a separate gas reservoir. The gas is a natural gas having, by mole fraction: 0.872 methane, 0.076 ethane, 0.031 propane, 0.008  
10      n-butane, 0.005 i-butane, 0.002 n-pentane, 0.002 i-pentane and 0.004 nitrogen. Gas consumption during the test is an indication of the level of hydrate formation. A lower gas consumption indicates better hydrate control.

For each test, an additive is dissolved into a 120  
15      milliliter sample of sea water having about 3.5 weight percent dissolved salt. The sea water/additive solution is then placed into the autoclave and subjected to increased pressure at a temperature of 39.2°C for 20 hours. Gas consumption is monitored. One test is performed using sea  
20      water with no additive for comparison purposes. Results of the tests are shown in Table 1.

-50-

TABLE 1

Additive	Additive Concentration (wt %)	Gas Consumption (gram-mole)	
		1000 psig	2000 psig
None	---	0.5	0.6-0.7
PVP <sup>(1)</sup>	0.5	0.6	
PVCAP <sup>(2)</sup>	0.5	0.15	
VC-713	0.5	0.10	
PNEAM <sup>(3)</sup>	0.5	0.12	
PNNDMAM <sup>(4)</sup>	0.5	0.17	
VC-713/ PNEAM <sup>(5)</sup>	0.5/0.5	.	0.12
PVCAP/PNEAM <sup>(6)</sup>	0.5/0.5		0.37

(1) Poly(N-vinyl-2-pyrrolidone)

(2) Poly(N-vinyl-ε-caprolactam)

(3) Poly(N-ethyl acrylamide)

(4) Poly(N,N-dimethylacrylamide)

(5) Mixture of VC-713 and poly(N-ethyl acrylamide)

(6) Mixture of poly(N-vinyl-ε-caprolactam) and poly(N-ethyl acrylamide)

The effectiveness at 2000 psi and 39.2°F demonstrated by the mixture of poly(N-ethyl acrylamide) with each of VC-713 and poly(N-vinyl-ε-caprolactam) is surprising considering that none of those additives used alone have been found to work effectively under those conditions. A synergistic effect seems to be obtained by combining the additives.

Example 5

This example illustrates the use of a poly(N-vinyl alkyl amide) alone and in combination with a poly(N-vinyl lactam).

-51-

The experimental procedure of Example 1 is repeated using 1 weight percent methanol and 0.50 weight percent poly(N-methyl-N-vinylacetamide). The solution becomes cloudy after about 3 minutes of rotating in the water bath.

5 After 12 hours of rotating in the water bath, the ball is still rolling, indicating an inhibition of hydrate formation and/or agglomeration.

The experiment is then repeated, except using 0.25 weight percent of poly(N-methyl-N-vinylacetamide) and 0.25  
10 weight percent of poly (N-vinyl- $\epsilon$ -caprolactam) instead of 0.5 weight percent of poly(N-methyl-N-vinylacetamide). The solution does not become cloudy over a 24 hour test period, indicating significantly enhanced performance of the mixture for clathrate hydrate control.

15 It should be recognized that any feature of any embodiment disclosed herein can be combined with any other feature of any other embodiment in any combination. Any additives can be used alone or in combination with one or more other additives. Any additive can be used as a primary  
20 additive or a secondary additive. Any functional group can be combined with any other functional group, either in a mixture or in a copolymer. While various embodiments of the present invention have been described in detail, it is apparent that modifications and adaptations of those  
25 embodiments will occur to those skilled in the art. It is to be expressly understood, however, that such modifications and adaptations are within the scope of the present invention.

-52-

What is claimed is:

1. A method for controlling problems that could occur in a fluid from the possible presence of a clathrate hydrate, the method comprising the steps of:

5 providing a flowable fluid that is susceptible to having a clathrate hydrate;

providing an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid;

10 contacting said fluid with said additive, wherein said additive comprises a polymer having at least some of a repeating unit with an amide comprising a nitrogen covalently bonded to a carbonyl carbon, and wherein attached to at least one of said nitrogen and said carbonyl 15 carbon of said amide is at least one organic group having from one to four carbon atoms.

2. The method of Claim 1, wherein:

said amide is a noncyclic amide.

3. The method of Claim 1, wherein:

20 said polymer comprises a backbone; and  
at least one of said nitrogen and said carbonyl carbon are part of a pendent constituent attached to and extending from said backbone.

4. The method of Claim 3, wherein:

25 both of said nitrogen and said carbonyl carbon are part of said pendent constituent.

-53-

5. The method of Claim 4, wherein:

said nitrogen occupies a position in said pendent constituent that is closer to said backbone than is the position occupied by said carbonyl carbon in said pendent constituent.

5

6. The method of Claim 4, wherein:

said carbonyl carbon occupies a position in said pendent constituent that is closer to said backbone than is the position occupied by said nitrogen in said pendent constituent.

10

7. The method of Claim 1, wherein:

said at least one organic group is an alkyl group.

8. The method of Claim 1, wherein:

each of said at least one organic group is independently selected from the group consisting of methyl, ethyl and propyl.

15

9. The method of Claim 1, wherein:

said repeating unit is representative of polymerizing an oxazoline.

20

10. The method of Claim 1, wherein:

said repeating unit is representative of polymerizing an ethylenically unsaturated monomer having an N-substituted amide.

11. The method of Claim 1, wherein:

25 said repeating unit is representative of polymerizing an N-substituted acrylamide.

-54-

12. The method of Claim 1, wherein:

said repeating unit is representative of polymerizing an ethylenically unsaturated monomer having an alkyl amide.

13. The method of Claim 1, wherein:

5 said repeating unit is representative of polymerizing an N-vinyl alkyl amide.

14. The method of Claim 1, wherein:

said repeating unit is representative of polymerizing at least one of the monomers selected from the group 10 consisting of 2-methyl-2-oxazoline, 2-ethyl-2-oxazoline, N-ethyl acrylamide, N-isopropyl acrylamide, N,N-dimethylacrylamide, N-vinylacetamide, and N-methyl-N-vinylacetamide.

15. The method of Claim 1, wherein:

15 said additive further comprises an organic ring.

16. The method of Claim 15, wherein:

said organic ring is a heterocyclic organic ring comprising nitrogen as a hetero atom.

17. The method of Claim 15, wherein:

20 said organic ring is a heterocyclic organic ring comprising an internal amide.

18. The method of Claim 15, wherein:

said heterocyclic organic ring comprises at least one of a pyrrolidone ring structure and a caprolactam ring 25 structure.

19. The method of Claim 15, wherein:

said organic ring and said amide are both part of said polymer.

-55-

20. The method of Claim 15, wherein:

said additive comprises a first polymer having said organic ring and a second polymer having said amide.

21. A method for controlling problems that could occur in a fluid from the possible presence of a clathrate hydrate, the method comprising the steps of:

providing a fluid that is susceptible to having a clathrate hydrate;

10 providing an additive useful for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid; and

15 contacting said fluid with said additive, wherein said additive comprises a heterocyclic organic ring having nitrogen as a hetero atom in said heterocyclic organic ring and wherein said additive further comprises an amide group that is external to said heterocyclic organic ring.

22. The method of Claim 21, wherein:

said heterogenic organic ring comprises an amide linkage internal to said organic ring.

20 23. The method of Claim 21, wherein:

said heterocyclic organic ring comprises a 5 member ring.

24. The method of Claim 21, wherein:

25 said heterocyclic organic ring comprises a pyrrolidone ring structure.

25. The method of Claim 21, wherein:

said heterocyclic organic ring comprises a 7 member ring.

-56-

26. The method of Claim 21, wherein:

said heterocyclic organic ring comprises a caprolactam ring structure.

27. The method of Claim 21, wherein:

5 said additive comprises a polymer having a backbone and a pendent constituent that is attached to and extends from said backbone; and

said amide group forms at least part of said pendent constituent.

10 28. The method of Claim 21, wherein:

said additive comprises a polymer having at least some repeating units representative of polymerizing an ethylenically unsaturated monomer comprising said pendent constituent.

15 29. The method of Claim 21, wherein:

said additive comprises a polymer having at least some repeating units representative of polymerizing an acrylamide monomer.

30. The method of Claim 21, wherein:

20 said additive comprises a polymer having at least some repeating units representative of polymerizing an N-substituted acrylamide.

31. The method of Claim 21, wherein:

25 said additive comprises a polymer having at least some repeating units representative of polymerizing an N-substituted acrylamide with at least one substituent that comprises from one to 3 carbon atoms.

-57-

32. The method of Claim 21, wherein:

said additive comprises a polymer having at least some repeating units representative of polymerizing at least one of N-ethyl acrylamide, N-isopropyl acrylamide and N,N-dimethylacrylamide.

33. The method of Claim 21, wherein:

said additive comprises a polymer having at least some repeating units representative of polymerizing an oxazoline compound.

10 34. The method of Claim 21, wherein:

said additive comprises a polymer having at least some repeating units representation of polymerizing at least one of 2-methyl-2-oxazoline and 2-ethyl-2-oxazoline.

35. The method of Claim 21, wherein:

15 said additive comprises a polymer having at least some repeating units representative of polymerizing an N-vinyl alkyl amide compound.

36. The method of Claim 21, wherein:

20 said additive comprises a polymer having at least some repeating units representative of polymerizing at least one of N-methyl-N-vinylacetamide, N-vinylacetamide and N-vinylformamide.

37. The method of Claim 21, wherein:

25 said additive comprises a polymer having at least some of a first repeating unit comprising said heterocyclic organic ring and at least some of a second repeating unit comprising said amide group.

-58-

38. The method of Claim 21, wherein:

said additive comprises a polymer having at least some repeating units representative of polymerizing at least one of N-vinyl-2-pyrrolidone and N-vinyl- $\epsilon$ -caprolactam.

5 39. The method of Claim 21, wherein:

said additive comprises a first polymer having at least some of a first repeating unit comprising said organic ring; and

10 said additive comprises a second polymer comprising at least some of a second repeating unit comprising said amide group.

40. The method of Claim 39, wherein:

said organic ring of said first polymer is a first organic ring; and

15 said amide group of said second polymer is internal to a second organic ring.

41. The method of Claim 40, wherein:

said first organic ring comprises an amide internal to said first organic ring; and

20 said first organic ring is different than said second organic ring.

42. The method of Claim 39, wherein:

said second polymer further comprises an ionic group.

43. The method of Claim 42, wherein:

25 said ionic group comprises at least one of a sulfonate group, a sulfinate group, a phosphate group, a phosphinate group, a phosphate group, and a carboxylate group.

-59-

44. A method for controlling problems that could occur in a fluid from the possible presence of a clathrate hydrate, the method comprising the steps of:

providing a fluid that is susceptible to having a  
5 clathrate hydrate;

providing an additive useful for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid; and

10 contacting said fluid with said additive, wherein said additive comprises a polymer having a backbone and a pendent constituent which is attached to and extends from said backbone and which comprises a noncyclic N-substituted amide.

45. The method of Claim 44, wherein:

15 said N-substituted amide comprises an alkyl substituent attached to the nitrogen atom of said N-substituted amide.

46. The method of Claim 44, wherein:

said N-substituted amide is a N-monosubstituted amide.

20 47. The method of Claim 44, wherein:

said N-substituted amide is an N,N-disubstituted amide.

48. The method of Claim 44, wherein:

25 said polymer comprises at least some repeating units representative of polymerizing an ethylenically unsaturated monomer comprising said pendent constituent.

-60-

49. The method of Claim 44, wherein:

said polymer comprises at least some repeating units representative of polymerizing an N-substituted acrylamide.

50. The method of Claim 44, wherein:

5 said polymer comprises at least some repeating units representative of polymerizing at least one of N-ethyl acrylamide, N-isopropyl acrylamide and N,N-dimethylacrylamide.

51. The method of Claim 44, wherein:

10 said polymer comprises at least some repeating units representative of polymerizing an N-substituted acrylamide having a C<sub>3</sub> alkyl group attached to the nitrogen atom of said N-substituted amide.

15 52. A method for controlling problems that could occur in a fluid from the possible presence of a clathrate hydrate, the method comprising the steps of:

providing a flowable fluid that is susceptible to having a clathrate hydrate;

20 providing an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in the fluid;

25 contacting said fluid with said additive, wherein said additive comprises a polymer having a backbone and a pendent constituent attached to and extending from said backbone, wherein said pendent constituent has an amide that comprises a nitrogen covalently bonded with a carbonyl carbon, and wherein said nitrogen occupies a position within said pendent constituent that is closer to the

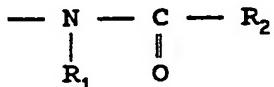
-61-

backbone than is the position occupied by said carbonyl carbon within said pendent constituent.

53. The method of Claim 52, wherein:

said pendent constituent comprises the chemical group

5



wherein  $\text{R}_1$  and  $\text{R}_2$  are independently hydrogen or an organic group.

10 54. The method of Claim 52, wherein:

at least one of  $\text{R}_1$  and  $\text{R}_2$  is an alkyl group.

55. The method of Claim 52, wherein:

said polymer comprises at least some of a repeating unit representative of polymerizing an ethylenically unsaturated monomer having said pendent group.

15 56. The method of Claim 52, wherein:

said polymer comprises at least some of a repeating unit representative of polymerizing an N-vinyl alkyl amide.

57. The method of Claim 52, wherein:

20 said polymer comprises at least some of a repeating unit representative of polymerizing at least one of N-methyl-N-vinylacetamide, N-vinylacetamide and N-vinylformamide.

25 58. A method for controlling clathrate hydrates in a fluid, the method comprising the steps of:

providing a flowable fluid comprising water and a guest molecule that is susceptible to formation of a clathrate hydrate; and

-62-

contacting said fluid with an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate;

wherein said additive comprises a polymer having at 5 least some repeating units characteristic of polymerizing an oxazoline.

59. The method of Claim 58, wherein:

said oxazoline comprises a 2-oxazoline.

60. The method of Claim 58, wherein:

10 said oxazoline comprises at least one of 2-ethyl-2-oxazoline and 2-methyl-2-oxazoline.

61. A method for controlling clathrate hydrates in a fluid, the method comprising the steps of:

15 providing a flowable fluid comprising water and a guest molecule that is susceptible to formation of a clathrate hydrate; and

contacting said fluid with an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid;

20 wherein said additive comprises a polymer with a first constituent having an organic ring and a second constituent having an ionic group.

62. The method of Claim 61, wherein:

25 said organic ring of said first constituent is a heterocyclic ring comprising nitrogen as a hetero atom.

63. The method of Claim 61, wherein:

said organic ring of said first constituent comprises an amide linkage internal to said organic ring.

-63-

64. The method of Claim 61, wherein:  
said ionic group is anionic.

65. The method of Claim 61, wherein:  
said ionic group comprises at least one of a sulfonate  
5 group, a sulfinate group, a sulfate group, a phosphonate  
group, a phosphinate group, a phosphate group and a  
carboxylate group.

66. The method of Claim 61, wherein:  
said ionic group comprises a 2-acrylamide-2-propane  
10 sulfonate.

67. The method of Claim 61, wherein:  
said polymer has a backbone chain, and wherein said  
first constituent and said second constituent are  
independently pendent from said backbone chain, such that  
15 said organic ring does not form part of said backbone chain  
and said ionic group is not attached to said ring.

68. The method of Claim 61, wherein:  
said polymer comprises first repeating units  
characteristic of polymerizing an ethylenically unsaturated  
20 first monomer having a lactam ring and second repeating  
units characteristic of polymerizing an ethylenically  
unsaturated second monomer having an ionic group.

69. The method of Claim 68, wherein:  
said first monomer comprises an N-vinyl lactam.  
25 70. The method of Claim 68, wherein:  
said polymer comprises third repeating units  
characteristic of polymerizing an acrylamide monomer.

-64-

71. The method of Claim 70, wherein:

said first monomer comprises N-vinyl-2-pyrrolidone,  
said second monomer comprises sodium 2-acrylamido-2-propane  
sulfonate, and said third monomer comprises acrylamide.

5 72. A method for controlling clathrate hydrates in a  
fluid, the method comprising the steps of:

providing a flowable fluid comprising water and a  
guest molecule that is susceptible to formation of a  
clathrate hydrate; and

10 contacting said fluid with an additive for reducing  
the potential for problems that could be caused by the  
presence of a clathrate hydrate in said fluid;

wherein said additive comprises a polymer having a  
backbone chain and a plurality of constituents pendent from  
15 said backbone, said constituents comprising an organic  
ring; and

wherein said additive further comprises means for  
reducing the tendency of said organic rings to associate  
with one another in an aqueous solution.

20 73. The method of Claim 72, wherein:

said means for reducing the tendency of said organic  
rings to associate with one another in an aqueous solution  
comprises sterically hindering association of said rings.

74. The method of Claim 72, wherein:

25 said means for reducing the tendency of said organic  
rings to associate with one another in an aqueous solution  
comprises charge repulsion.

-65-

75. The method of Claim 72, wherein:

said organic ring comprises an amide linkage internal to said organic ring.

76. A method for controlling clathrate hydrates in a  
5 fluid, the method comprising the steps of:

providing a flowable fluid comprising water and a guest molecule that is susceptible to formation of a clathrate hydrate; and

10 contacting said fluid with an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid;

wherein said additive comprises a polymer having a molecular weight of greater than about one million.

77. The method of Claim 76, wherein:

15 said polymer comprise first repeating units having an organic ring and second repeating units not having an organic ring.

78. The method of Claim 76, wherein:

20 said organic ring has an amide linkage internal to the ring.

79. The method of Claim 76, wherein:

said second repeating unit is representative of polymerizing an acrylamide monomer.

80. The method of Claim 76, wherein:

25 said first repeating units are representative of polymerizing an N-vinyl lactam and said second repeating units are representative of polymerizing an acrylamide monomer.

-66-

81. A method for controlling problems that could occur in a fluid from the possible presence of a clathrate hydrate, the method comprising the steps of:

5 providing a flowable fluid that has first clathrate hydrate masses therein which are susceptible to agglomeration to form second, larger clathrate hydrate masses which could block or detrimentally impair flow of said fluid;

10 providing an additive useful for reducing the tendency of clathrate hydrate masses to agglomerate;

15 contacting said fluid with said additive and flowing said fluid and said additive from a first location to a second location at a pressure of greater than about 1600 psia and a temperature of lower than about 45°F, wherein said first clathrate hydrate masses are prevented from agglomerating into said second clathrate hydrate masses to permit flowing of said fluid without blockage.

82. The method of Claim 81, wherein:

20 said step of flowing said fluid and said additive is at a pressure of greater than about 1900 psia.

83. The method of Claim 81, wherein:

said step of flowing said fluid and said additive is at a temperature of lower than about 40°F.

84. The method of Claim 81, wherein:

25 said additive comprises a polymer.

-67-

85. The method of Claim 81, wherein:

said fluid comprises water and said additive is added to said fluid in an amount that is less than about 1 weight percent relative to said water.

5 86. A method for controlling clathrate hydrates in a fluid, the method comprising the steps of:

providing a flowable fluid comprising water and a guest molecule that is susceptible to formation of a clathrate hydrate;

10 providing a first chemical compound;

providing a second chemical compound; and

contacting said fluid substantially simultaneously with said first chemical compound and said second chemical compound for reducing the potential for problems that could 15 be caused by a clathrate hydrate;

wherein, said first chemical compound comprises a polymer with an organic ring having an amide linkage internal to the ring and said second chemical compound comprises an alcohol.

20 87. The method of Claim 86, wherein:

said polymer has at least some repeating units characteristic of polymerizing an N-vinyl lactam.

88. The method of Claim 86, wherein:

said organic ring comprises a 2-pyrrolidone ring.

25 89. The method of Claim 86, wherein:

said organic ring comprises a  $\delta$ -valerolactam ring.

90. The method of Claim 86, wherein:

said organic ring comprises an  $\epsilon$ -caprolactam ring.

-68-

91. The method of Claim 86, wherein:

said second chemical compound is an alcohol that is soluble in water.

92. The method of Claim 86, wherein:

5 said second chemical compound is selected from the group consisting of methanol, ethanol and ethylene glycol.

93. The method of Claim 86, wherein:

10 said first chemical compound and said second chemical compound are mixed together prior to contacting said first chemical compound and said second chemical compound with said fluid.

94. The method of Claim 86, wherein:

said alcohol comprises an alcohol other than methanol.

95. A method for controlling clathrate hydrates in a 15 fluid, the method comprising the steps of:

providing a fluid comprising water and a guest molecule that is susceptible to formation of a clathrate hydrate; and

20 contacting said fluid with an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid;

wherein said additive comprises a copolymer consisting essentially of first repeating units characteristic of polymerizing N-vinyl-2-pyrrolidone and second repeating 25 units characteristic of polymerizing N-vinyl- $\epsilon$ -caprolactam.

96. The method of Claim 95, wherein:

said copolymer comprises greater than about 50 weight percent of said second repeating units.

-69-

97. The method of Claim 95, wherein:

said copolymer comprises greater than about 75 weight percent of said first repeating units.

98. A method for controlling clathrate hydrates in a  
5 fluid, the method comprising the steps of:

providing a fluid comprising water and a guest molecule that is susceptible to formation of a clathrate hydrate;

providing a first chemical compound;

10 providing a second chemical compound that is different than said first chemical compound; and

contacting said fluid substantially simultaneously with said first chemical compound and said second chemical compound;

15 wherein said first chemical compound comprises a first constituent having a first amide group and said second chemical compound comprises a second constituent having a second amide group.

99. The method of Claim 98, wherein:

20 said first amide group comprises an amide linkage internal to an organic ring.

100. The method of Claim 98, wherein:

said second amide group comprises an amide linkage internal to an organic ring.

25 101. The method of Claim 98, wherein:

said first constituent and said second constituent are independently selected from the group consisting of a

-70-

2-pyrrolidone ring, a  $\delta$ -valerolactam ring, and an  $\epsilon$ -caprolactam ring.

102. The method of Claim 98, wherein:

said second chemical compound comprises a plurality of  
5 ionic groups.

103. The method of Claim 98, wherein:

said first chemical compound is a polymer comprising  
a plurality of said first constituent and said second  
chemical compound is a polymer comprising a plurality of  
10 said second constituent.

104. The method of Claim 98, wherein:

said first chemical compound is a polymer comprising  
a plurality of said first constituents, said first  
constituents comprising an amide linkage internal to said  
ring, said first chemical compound further comprising a  
15 plurality of a third constituent comprising an ionic group;  
and

said second chemical compound comprises a plurality of  
said second constituent with said second amide group  
20 comprising an amide linkage internal to a ring.

105. The method of Claim 104, wherein:

said first chemical compound comprises a polymer  
having repeating units characteristic of copolymerizing at  
least N-vinyl- $\epsilon$ -caprolactam, sodium 2-acrylamido-2-methyl-  
25 1-propane-sulfonate and acrylamide.

-71-

106. The method of Claim 104, wherein:

said first chemical compound is a polymer having at least some repeating units characteristic of polymerizing N-vinyl- $\epsilon$ -caprolactam.

5 107. The method of Claim 104, wherein:

said second chemical compound comprises a polymer selected for the group consisting of a homopolymer of N-vinyl-2-pyrrolidone, a homopolymer of N-vinyl- $\epsilon$ -caprolactam, and a copolymer of N-vinyl-2-pyrrolidone and 10 N-vinyl- $\epsilon$ -caprolactam.

108. The method of Claim 98, wherein:

said second amide group is not internal to an organic ring.

109. The method of Claim 98, wherein:

15 said second chemical compound comprises a polymer having at least some repeating units characteristic of polymerizing an oxazoline monomer, an N-substituted acrylamide and an N-vinyl alkyl amide.

110. The method of Claim 98, wherein:

20 said second chemical compound comprises a polypeptide.

111. A polymer useful for controlling clathrate hydrates, said polymer comprising:

an organic backbone chain;

25 a plurality of a first constituent pendent from said backbone chain, said first constituent comprising a seven member organic ring; and

-72-

a plurality of a second constituent pendent from said backbone, said second constituent comprising an ionic group.

112. The polymer of Claim 111, wherein:

5       said organic backbone is characteristic of polymerizing ethylenically monounsaturated monomers.

113. The polymer of Claim 111, wherein:

      said seven-member organic ring comprises an  $\epsilon$ -caprolactam ring.

10      114. The polymer of Claim 111, wherein:

      said ionic group is an anionic group.

115. The polymer of Claim 111, wherein:

      said ionic group is an anionic group selected from the group consisting of a sulfonate, a sulfinate, a sulfate, a phosphonate, a phosphinate, a phosphate and a carboxylate.

15      116. The polymer of Claim 111, wherein:

      said polymer comprises a first repeating unit characteristic of polymerizing N-vinyl- $\epsilon$ -caprolactam and a second repeating unit characteristic of polymerizing a 2-acrylamido-2-methyl-1-propane sulfonate.

**AMENDED CLAIMS**

[received by the International Bureau on 30 November 1995 (30.11.95); original claims 2,3,77,94 and 96 cancelled; original claims 1,4,28,52,76,86, 92,95,98 and 100 amended; remaining claims unchanged (20 pages)]

1. A method for controlling problems that could occur in a fluid from the possible presence of a clathrate hydrate, the method comprising the steps of:
  - providing a flowable fluid that is susceptible to having a clathrate hydrate;
  - providing an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid;
  - contacting said fluid with said additive, wherein said additive comprises a polymer having at least some of a repeating unit with a noncyclic amide comprising a nitrogen covalently bonded to a carbonyl carbon, and wherein attached to at least one of said nitrogen and said carbonyl carbon of said amide is at least one organic group having from one to four carbon atoms; and  
wherein said polymer comprises a backbone, and at least one of said nitrogen and said carbonyl are part of a pendant constituent attached to and extending from said backbone.
20. 4. The method of Claim 1, wherein:  
both of said nitrogen and said carbonyl carbon are part of said pendant constituent.
5. The method of Claim 4, wherein:  
said nitrogen occupies a position in said pendent constituent that is closer to said backbone than is the position occupied by said carbonyl carbon in said pendent constituent.

-74-

6. The method of Claim 4, wherein:

said carbonyl carbon occupies a position in said pendent constituent that is closer to said backbone than is the position occupied by said nitrogen in said pendent constituent.

5

7. The method of Claim 1, wherein:

said at least one organic group is an alkyl group.

8. The method of Claim 1, wherein:

each of said at least one organic group is independently selected from the group consisting of methyl, 10 ethyl and propyl.

10

9. The method of Claim 1, wherein:

said repeating unit is representative of polymerizing an oxazoline.

15

10. The method of Claim 1, wherein:

said repeating unit is representative of polymerizing an ethylenically unsaturated monomer having an N-substituted amide.

20

11. The method of Claim 1, wherein:

said repeating unit is representative of polymerizing an N-substituted acrylamide.

25

12. The method of Claim 1, wherein:

said repeating unit is representative of polymerizing an ethylenically unsaturated monomer having an alkyl amide.

13. The method of Claim 1, wherein:

said repeating unit is representative of polymerizing an N-vinyl alkyl amide.

14. The method of Claim 1, wherein:

-75-

said repeating unit is representative of polymerizing at least one of the monomers selected from the group consisting of 2-methyl-2-oxazoline, 2-ethyl-2-oxazoline, N-ethyl acrylamide, N,N-dimethylacrylamide, N-vinylacetamide, 5 and N-methyl-N-vinylacetamide.

15. The method of Claim 1, wherein:

said additive further comprises an organic ring.

16. The method of Claim 15, wherein:

said organic ring is a heterocyclic organic ring 10 comprising nitrogen as a hetero atom.

17. The method of Claim 15, wherein:

said organic ring is a heterocyclic organic ring comprising an internal amide.

18. The method of Claim 15, wherein:

15 said heterocyclic organic ring comprises at least one of a pyrrolidone ring structure and a caprolactam ring structure.

19. The method of Claim 15, wherein:

20 said organic ring and said amide are both part of said polymer.

20. The method of Claim 15, wherein:

said additive comprises a first polymer having said organic ring and a second polymer having said amide.

21. A method for controlling problems that could 25 occur in a fluid from the possible presence of a clathrate hydrate, the method comprising the steps of:

providing a fluid that is susceptible to having a clathrate hydrate;

-76-

providing an additive useful for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid; and

5 contacting said fluid with said additive, wherein said additive comprises a heterocyclic organic ring having nitrogen as a hetero atom in said heterocyclic organic ring and wherein said additive further comprises an amide group that is external to said heterocyclic organic ring.

22. The method of Claim 21, wherein:

10 said heterogenic organic ring comprises an amide linkage internal to said organic ring.

23. The method of Claim 21, wherein:

said heterocyclic organic ring comprises a 5 member ring.

15 24. The method of Claim 21, wherein:

said heterocyclic organic ring comprises a pyrrolidone ring structure.

25. The method of Claim 21, wherein:

20 said heterocyclic organic ring comprises a 7 member ring.

26. The method of Claim 21, wherein:

said heterocyclic organic ring comprises a caprolactam ring structure.

27. The method of Claim 21, wherein:

25 said additive comprises a polymer having a backbone and a pendent constituent that is attached to and extends from said backbone; and

-77-

said amide group forms at least part of said pendent constituent.

28. The method of Claim 27, wherein:

said additive comprises a polymer having at least some  
5 repeating units representative of polymerizing an ethylenically unsaturated monomer comprising said pendent constituent.

29. The method of Claim 21, wherein:

said additive comprises a polymer having at least some  
10 repeating units representative of polymerizing an acrylamide monomer.

30. The method of Claim 21, wherein:

said additive comprises a polymer having at least some  
repeating units representative of polymerizing an N-  
15 substituted acrylamide.

31. The method of Claim 21, wherein:

said additive comprises a polymer having at least some  
repeating units representative of polymerizing an N-  
substituted acrylamide with at least one substituent that  
20 comprises from one to 3 carbon atoms.

32. The method of Claim 21, wherein:

said additive comprises a polymer having at least some  
repeating units representative of polymerizing at least one  
of N-ethyl acrylamide and N,N-dimethylacrylamide.

25 33. The method of Claim 21, wherein:

said additive comprises a polymer having at least some  
repeating units representative of polymerizing an oxazoline  
compound.

-78-

34. The method of Claim 21, wherein:

said additive comprises a polymer having at least some repeating units representative of polymerizing at least one of 2-methyl-2-oxazoline and 2-ethyl-2-oxazoline.

5 35. The method of Claim 21, wherein:

said additive comprises a polymer having at least some repeating units representative of polymerizing an N-vinyl alkyl amide compound.

36. The method of Claim 21, wherein:

10 said additive comprises a polymer having at least some repeating units representative of polymerizing at least one of N-methyl-N-vinylacetamide, N-vinylacetamide and N-vinylformamide.

37. The method of Claim 21, wherein:

15 said additive comprises a polymer having at least some of a first repeating unit comprising said heterocyclic organic ring and at least some of a second repeating unit comprising said amide group.

38. The method of Claim 21, wherein:

20 said additive comprises a polymer having at least some repeating units representative of polymerizing at least one of N-vinyl-2-pyrrolidone and N-vinyl- $\epsilon$ -caprolactam.

39. The method of Claim 21, wherein:

25 said additive comprises a first polymer having at least some of a first repeating unit comprising said organic ring; and

-79-

said additive comprises a second polymer comprising at least some of a second repeating unit comprising said amide group.

40. The method of Claim 39, wherein:

5 said organic ring of said first polymer is a first organic ring; and

said amide group of said second polymer is internal to a second organic ring.

41. The method of Claim 40, wherein:

10 said first organic ring comprises an amide internal to the ring; and

said first organic ring is different than said second organic ring.

42. The method of Claim 39, wherein:

15 said second polymer further comprises an ionic group.

43. The method of Claim 42, wherein:

said ionic group comprises at least one of a sulfonate group, a sulfinate group, a phosphate group, a phosphinate group, a phosphate group, and a carboxylate group.

20 44. A method for controlling problems that could occur in a fluid from the possible presence of a clathrate hydrate, the method comprising the steps of:

providing a fluid that is susceptible to having a clathrate hydrate;

25 providing an additive useful for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid; and

-80-

contacting said fluid with said additive, wherein said additive comprises a polymer having a backbone and a pendent constituent which is attached to and extends from said backbone and which comprises a noncyclic N-substituted amide.

5 45. The method of Claim 44, wherein:

said N-substituted amide comprises an alkyl substituent attached to the nitrogen atom of said N-substituted amide.

10 46. The method of Claim 44, wherein:

said N-substituted amide is a N-monosubstituted amide.

47. The method of Claim 44, wherein:

said N-substituted amide is an N,N-disubstituted amide.

15 48. The method of Claim 44, wherein:

said polymer comprises at least some repeating units representative of polymerizing an ethylenically unsaturated monomer comprising said pendent constituent.

49. The method of Claim 44, wherein:

20 said polymer comprises at least some repeating units representative of polymerizing an N-substituted acrylamide.

50. The method of Claim 44, wherein:

said polymer comprises at least some repeating units representative of polymerizing at least one of N-ethyl acrylamide and N,N-dimethylacrylamide.

25 51. The method of Claim 44, wherein:

said polymer comprises at least some repeating units representative of polymerizing an N-substituted acrylamide

-81-

having a  $C_3$  alkyl group attached to the nitrogen atom of said N-substituted amide.

52. A method for controlling problems that could occur in a fluid from the possible presence of a clathrate hydrate, the method comprising the steps of:

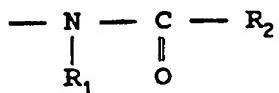
providing a flowable fluid that is susceptible to having a clathrate hydrate;

10 providing an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in the fluid;

15 contacting said fluid with said additive, wherein said additive comprises a polymer having a backbone and a pendent constituent attached to and extending from said backbone, wherein said pendent constituent has a noncyclic amide that comprises a nitrogen covalently bonded with a carbonyl carbon, and wherein said nitrogen occupies a position within said pendent constituent that is closer to the backbone than is the position occupied by said carbonyl carbon within said pendent constituent.

20 53. The method of Claim 52, wherein:

said pendent constituent comprises the chemical group



25 wherein  $R_1$  and  $R_2$  are independently hydrogen or an organic group.

54. The method of Claim 52, wherein:

at least one of  $R_1$  and  $R_2$  is an alkyl group.

55. The method of Claim 52, wherein:

-82-

said polymer comprises at least some of a repeating unit representative of polymerizing an ethylenically unsaturated monomer having said pendent group.

56. The method of Claim 52, wherein:

5 said polymer comprises at least some of a repeating unit representative of polymerizing an N-vinyl alkyl amide.

57. The method of Claim 52, wherein:

10 said polymer comprises at least some of a repeating unit representative of polymerizing at least one of N-methyl-N-vinylacetamide, N-vinylacetamide and N-vinylformamide.

58. A method for controlling clathrate hydrates in a fluid, the method comprising the steps of:

15 providing a flowable fluid comprising water and a guest molecule that is susceptible to formation of a clathrate hydrate; and

contacting said fluid with an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate;

20 wherein said additive comprises a polymer having at least some repeating units characteristic of polymerizing an oxazoline.

59. The method of Claim 58, wherein:

said oxazoline comprises a 2-oxazoline.

25 60. The method of Claim 58, wherein:

said oxazoline comprises at least one of 2-ethyl-2-oxazoline and 2-methyl-2-oxazoline.

61. A method for controlling clathrate hydrates in a fluid, the method comprising the steps of:

-83-

providing a flowable fluid comprising water and a guest molecule that is susceptible to formation of a clathrate hydrate; and

5 contacting said fluid with an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid;

wherein said additive comprises a polymer with a first constituent having an organic ring and a second constituent having a plurality of an ionic group.

10 62. The method of Claim 61, wherein:

said organic ring of said first constituent is a heterocyclic ring comprising nitrogen as a hetero atom.

63. The method of Claim 61, wherein:

said organic ring of said first constituent comprises 15 an amide linkage internal to said organic ring.

64. The method of Claim 61, wherein:

said ionic group is anionic.

65. The method of Claim 61, wherein:

said ionic group comprises at least one of a sulfonate 20 group, a sulfinate group, a sulfate group, a phosphonate group, a phosphinate group, a phosphate group and a carboxylate group.

66. The method of Claim 61, wherein:

said ionic group comprises a 2-acrylamide-2-propane 25 sulfonate.

67. The method of Claim 61, wherein:

said polymer has a backbone chain, and wherein said first constituent and said second constituent are independently pendent from said backbone chain, such that

-84-

said organic ring does not form part of said backbone chain and said ionic group is not attached to said ring.

68. The method of Claim 61, wherein:

5       said polymer comprises first repeating units characteristic of polymerizing an ethylenically unsaturated first monomer having a lactam ring and second repeating units characteristic of polymerizing an ethylenically unsaturated second monomer having an ionic group.

69. The method of Claim 68, wherein:

10      said first monomer comprises an N-vinyl lactam.

70. The method of Claim 68, wherein:

      said polymer comprises third repeating units characteristic of polymerizing an acrylamide monomer.

71. The method of Claim 70, wherein:

15      said first monomer comprises N-vinyl-2-pyrrolidone, said second monomer comprises sodium 2-acrylamido-2-propane sulfonate, and said third monomer comprises acrylamide.

72. A method for controlling clathrate hydrates in a fluid, the method comprising the steps of:

20      providing a flowable fluid comprising water and a guest molecule that is susceptible to formation of a clathrate hydrate; and

      contacting said fluid with an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid;

25      wherein said additive comprises a polymer having a backbone chain and a plurality of constituents pendent from said backbone, said constituents comprising an organic ring; and

-85-

wherein said additive further comprises means for reducing the tendency of said organic rings to associate with one another in an aqueous solution.

73. The method of Claim 72, wherein:

5 said means for reducing the tendency of said organic rings to associate with one another in an aqueous solution comprises sterically hindering association of said rings.

74. The method of Claim 72, wherein:

10 said means for reducing the tendency of said organic rings to associate with one another in an aqueous solution comprises charge repulsion.

75. The method of Claim 72, wherein:

said organic ring comprises an amide linkage internal to said organic ring.

15 76. A method for controlling clathrate hydrates in a fluid, the method comprising the steps of:

providing a flowable fluid comprising water and a guest molecule that is susceptible to formation of a clathrate hydrate; and

20 contacting said fluid with an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid;

wherein said additive comprises a polymer having a molecular weight of greater than about one million; and

25 wherein, said polymer comprises first repeating units having an organic ring and second repeating units not having an organic ring.

78. The method of Claim 76, wherein:

30 said organic ring has an amide linkage internal to the ring.

-86-

79. The method of Claim 76, wherein:

said second repeating unit is representative of polymerizing an acrylamide monomer.

80. The method of Claim 76, wherein:

5 said first repeating units are representative of polymerizing an N-vinyl lactam and said second repeating units are representative of polymerizing an acrylamide monomer.

10 81. A method for controlling problems that could occur in a fluid from the possible presence of a clathrate hydrate, the method comprising the steps of:

15 providing a flowable fluid that has first clathrate hydrate masses therein which are susceptible to agglomeration to form second, larger clathrate hydrate masses which could block or detrimentally impair flow of said fluid;

providing an additive useful for reducing the tendency of clathrate hydrate masses to agglomerate;

20 contacting said fluid with said additive and flowing said fluid and said additive from a first location to a second location at a pressure of greater than about 1600 psia and a temperature of lower than about 45°F, wherein said first clathrate hydrate masses are prevented from agglomerating into said second clathrate hydrate masses to permit said flowing of said fluid without blockage.

25 82. The method of Claim 81; wherein:

said step of flowing said fluid and said additive is at a pressure of greater than about 1900 psia.

83. The method of Claim 81, wherein:

-87-

said step of flowing said fluid and said additive is at a temperature of lower than about 40°F.

84. The method of Claim 81, wherein:  
said additive comprises a polymer.

5 85. The method of Claim 81, wherein:

said fluid comprises water and said additive is added to said fluid in an amount that is less than about 1 weight percent relative to said water.

86. A method for controlling clathrate hydrates in a  
10 fluid, the method comprising the steps of:

providing a flowable fluid comprising water and a guest molecule that is susceptible to formation of a clathrate hydrate;

providing a first chemical compound;

15 providing a second chemical compound; and

contacting said fluid substantially simultaneously with said first chemical compound and said second chemical compound for reducing the potential for problems that could be caused by a clathrate hydrate;

20 wherein, said first chemical compound comprises a polymer with an organic ring having an amide linkage internal to the ring and said second chemical compound comprises an alcohol other than methanol.

87. The method of Claim 81, wherein:  
25 said polymer has at least some repeating units characteristic of polymerizing an N-vinyl lactam.

88. The method of Claim 86, wherein:

said organic ring comprises a 2-pyrrolidone ring.

89. The method of Claim 86, wherein:  
30 said organic ring comprises a  $\delta$ -valerolactam ring.

-88-

90. The method of Claim 86, wherein:

said organic ring comprises an  $\epsilon$ -caprolactam ring.

91. The method of Claim 86, wherein:

said second chemical compound is an alcohol that is

5 soluble in water.

92. The method of Claim 86, wherein:

said second chemical compound is selected from the group consisting of ethanol and ethylene glycol.

93. The method of Claim 86, wherein:

10 said first chemical compound and said second chemical compound are mixed together prior to contacting said first chemical compound and said second chemical compound with said fluid.

95. A method for controlling clathrate hydrates in a  
15 fluid, the method comprising the steps of:

providing a fluid comprising water and a guest molecule that is susceptible to formation of a clathrate hydrate; and

20 contacting said fluid with an additive for reducing the potential for problems that could be caused by the presence of a clathrate hydrate in said fluid;

wherein said additive comprises a copolymer consisting essentially of first repeating units characteristic of polymerizing N-vinyl-2-pyrrolidone and second repeating units characteristic of polymerizing N-vinyl- $\epsilon$ -caprolactam, and wherein said copolymer comprises greater than about 50 weight percent of said second repeating unit.

97. The method of Claim 95, wherein:

30 said copolymer comprises greater than about 75 weight percent of said first repeating units.

-89-

98. A method for controlling clathrate hydrates in a fluid, the method comprising the steps of:

providing a fluid comprising water and a guest molecule that is susceptible to formation of a clathrate  
5 hydrate;

providing a first chemical compound;

providing a second chemical compound that is different than said first chemical compound; and

10 contacting said fluid substantially simultaneously with said first chemical compound and said second chemical compound;

wherein said first chemical compound comprises a first constituent having a first amide group and said second chemical compound comprises a second constituent having a  
15 second amide group.

99. The method of Claim 98, wherein:

said first amide group comprises an amide linkage internal to an organic ring.

100. The method of Claim 99, wherein:

20 said second amide group comprises an amide linkage internal to an organic ring.

101. The method of Claim 98, wherein:

25 said first constituent and said second constituent are independently selected from the group consisting of a 2-pyrrolidone ring, a  $\delta$ -valerolactam ring, and an  $\epsilon$ -caprolactam ring.

102. The method of Claim 98, wherein:

said second chemical compound comprises a plurality of ionic groups.

30 103. The method of Claim 98, wherein:

-90-

said first chemical compound is a polymer comprising a plurality of said first constituent and said second chemical compound is a polymer comprising a plurality of said second constituent.

5 104. The method of Claim 98, wherein:

said first chemical compound is a polymer comprising a plurality of said first constituents, said first constituents comprising an amide linkage internal to said ring, said first chemical compound further comprising a 10 plurality of a third constituent comprising an ionic group; and

said second chemical compound comprises a plurality of said second constituent with said second amide group comprising an amide linkage internal to a ring.

15 105. The method of Claim 104, wherein:

said first chemical compound comprises a polymer having repeating units characteristic of copolymerizing at least N-vinyl- $\epsilon$ -caprolactam, sodium 2-acrylamido-2-methyl-1-propane-sulfonate and acrylamide.

20 106. The method of Claim 104, wherein:

said first chemical compound is a polymer having at least some repeating units characteristic of polymerizing N-vinyl- $\epsilon$ -caprolactam.

107. The method of Claim 104, wherein:

25 said second chemical compound comprises a polymer selected for the group consisting of a homopolymer of N-vinyl-2-pyrrolidone, a homopolymer of N-vinyl- $\epsilon$ -caprolactam, and a copolymer of N-vinyl-2-pyrrolidone and N-vinyl- $\epsilon$ -caprolactam.

30 108. The method of Claim 98, wherein:

-91-

said second amide group is not internal to an organic ring.

109. The method of Claim 98, wherein:

said second chemical compound comprises a polymer  
5 having at least some repeating units characteristic of polymerizing an oxazoline monomer, an N-substituted acrylamide and an N-vinyl alkyl amide.

110. The method of Claim 98, wherein:

said second chemical compound comprises a polypeptide.

111. A polymer useful for controlling clathrate hydrates, said polymer comprising:

an organic backbone chain;

a plurality of a first constituent pendent from said backbone chain, said first constituent comprising a seven member organic ring; and

15 a plurality of a second constituent pendent from said backbone, said second constituent comprising an ionic group.

112. The polymer of Claim 111, wherein:

20 said organic backbone is characteristic of polymerizing ethylenically monounsaturated monomers.

113. The polymer of Claim 111, wherein:

said seven-member organic ring comprises an  $\epsilon$ -caprolactam ring.

25 114. The polymer of Claim 111, wherein:

said ionic group is an anionic group.

115. The polymer of Claim 111, wherein:

said ionic group is an anionic group selected from the group consisting of a sulfonate, a sulfinate, a sulfate, a phosphonate, a phosphinate, a phosphate and a carboxylate.

-92-

116. The polymer of Claim 111, wherein:

said polymer comprises a first repeating unit  
characteristic of polymerizing N-vinyl- $\epsilon$ -caprolactam and a  
second repeating unit characteristic of polymerizing a 2-  
5 acrylamido-2-methyl-1-propane sulfonate.

## INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/US 95/06042

A. CLASSIFICATION OF SUBJECT MATTER					
IPC 6	E21B37/06	C10L3/00	F15D1/00	F17D1/05	F17D1/02
	C09K7/06	C08F228/02	C08F226/06	F17D1/00	

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 E21B C10L F15D C09K C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO-A-94 25727 (BP ) 10 November 1994  see the whole document ---	1,3-5, 21-28, 52, 61-65, 67-69, 72-78, 86-94, 98,100, 102
X	US,A,4 915 176 (SUGIER ET AL.) 10 April 1990 cited in the application see column 2, line 46 - column 3, line 38 --- -/-	1,2,21, 23,98, 110

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

1 September 1995

Date of mailing of the international search report

11.09.1995

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl.  
Fax (+ 31-70) 340-3016

Authorized officer

De La Morinerie, B

## INTERNATIONAL SEARCH REPORT

Internat'l Application No  
PCT/US 95/06042

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO,A,95 19408 (BP) 20 July 1995  see the whole document ---	1,3,4,6, 21-28, 38-43, 52, 61-65, 67-69, 72-76, 86-95, 98-104, 108,110
X	WO,A,93 25798 (SHELL) 23 December 1993 cited in the application  see claims 1,10 ---	21,23, 52,72, 73,75,76
P,X	WO,A,94 12761 (COLORADO SCHOOL OF MINES) 9 June 1994 cited in the application  see page 13 - page 18 ---	1,3-5, 10, 15-19, 21-28, 37,38, 52, 61-63, 72-75, 86-93,95
X	US,A,4 132 535 (RIVERS ET AL.) 2 January 1979 see column 1 - column 2 ---	61,72-74
X	EP,A,0 115 836 (PHILLIPS PETROLEUM COMP.) 15 August 1984 see the whole document ---	111-116
X	WO,A,83 02449 (CASSELLA) 21 July 1983 see the whole document ---	111-116
A	DE,A,34 39 797 (EXXON) 9 May 1985 see the whole document ---	1-116
A	US,A,4 609 476 (HEILWEIL) 2 September 1986 see the whole document ---	1-116
A	FR,A,2 238 130 (DOW) 14 February 1975 see the whole document ---	1-116
A	US,A,3 768 565 (PERSINSKI ET AL.) 30 October 1973  see the whole document -----	1-8, 10-14, 44-51

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Inventor / Application No

PCT/US 95/06042

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9425727	10-11-94	NONE		
US-A-4915176	10-04-90	FR-A- EP-A, B JP-A-	2625527 0323307 2030883	07-07-89 05-07-89 01-02-90
WO-A-9519408	20-07-95	NONE		
WO-A-9325798	23-12-93	AU-B-	4325993	04-01-94
WO-A-9412761	09-06-94	US-A- US-A- AU-B- EP-A- NO-A-	5432292 5420370 5612194 0668958 951999	11-07-95 30-05-95 22-06-94 30-08-95 19-05-95
US-A-4132535	02-01-79	NONE		
EP-A-115836	15-08-84	US-A- US-A- AU-B- AU-A- CA-A- DE-D- DE-T- US-A- US-A- US-A- US-A-	4644020 4951921 553817 2372384 1254026 3486230 3486230 5080809 5186257 5326854 5382371	17-02-87 28-08-90 31-07-86 02-08-84 16-05-89 25-11-93 17-02-94 14-01-92 16-02-93 05-07-94 17-01-95
WO-A-8302449	21-07-83	US-A- AU-A- EP-A-	4471097 1019483 0111486	11-09-84 28-07-83 27-06-84
DE-A-3439797	09-05-85	US-A- US-A- CA-A- JP-C- JP-A- US-A-	4489180 4517333 1225184 1864307 60123534 4970260	18-12-84 14-05-85 04-08-87 08-08-94 02-07-85 13-11-90

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

Internat'l Application No  
PCT/US 95/06042

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE-A-3439797		US-A-	4536539	20-08-85
US-A-4609476	02-09-86	NONE		
FR-A-2238130	14-02-75	CA-A- DE-A- GB-A- SE-B- SE-A- US-A- US-A-	1031556 2433198 1466284 407522 7409413 4501775 4117214	23-05-78 06-02-75 02-03-77 02-04-79 20-01-75 26-02-85 26-09-78
US-A-3768565	30-10-73	CA-A-	985891	23-03-76